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RAY T. BAYLESS, *Editor*

Vol. XX **December, 1932** **No. 6**

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THE ROLE OF NICKEL IN NITRIDING STEELS

By H. J. French and V. O. Homerberg

Abstract

The data in this paper, taken from extended studies of many alloy steel systems, show that nickel may serve a useful role in nitriding steels.[1] *Its principal benefits are found in its strengthening and toughening effects upon the nitride case, its strengthening and hardening effects upon the core by which to provide better support to the case, and its development of dispersion hardening phenomena in steels containing appreciable proportions of aluminum by which an automatic increase in core strength and elastic properties is obtained during the nitriding cycle.*

As the result of these effects, nickel may be added in varying and regulated proportions to nitriding steels to control the toughness-hardness relations of the case and core and provide a wide range of properties to meet varied service requirements.

A number of low carbon nitriding steels are described in which the beneficial effects of nickel are realized by suitable combinations of nickel with other alloying elements. The case and core properties of these new steels are given in detail.

I. Introduction

THERE are now on the American markets a number of alloy steels intended especially for nitriding, the most important of which contain aluminum, chromium, molybdenum and vanadium in varying amounts and in different combinations. Typical compositions, suggested nitriding temperatures and case hardnesses obtainable are illustrated in Table I.

Nickel does not appear as an essential constituent of any of

[1]The present development is covered by patent protection.

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. Of the authors, H. J. French is in charge, alloy steel and iron development, The International Nickel Co., Inc., New York, V. O. Homberg is associate professor of physical metallurgy, Massachusetts Institute of Technology, Cambridge, Mass. Manuscript received July 29, 1932.

Table I
Commercial Steels for Nitriding (Typical Compositions and Data)

Present trade designation	Nitralloy 125 and 135	Nitralloy 225	Nitralloy 630	Nitralloy L	Nitrard No. 1
C	to suit	0.3	0.3	0.7	1.5
Mn	0.5	0.5	0.6	0.5	0.2
Al	1	1.2	..	1	..
Cr	1.3	..	1.5	1.25	12
Mo	0.2	0.8	..	0.75	1
V	..	..	0.5	0.15	1
W	..	..	..	1	..
Recommended nitriding temperature of	950-975	950-975	860	950-975	950-975
Approximate maximum case hardness (48 hr. treatment)	1050	975	875	1050	1100+
Purpose or outstanding qualities claimed	general purpose	general purpose	aimed for toughness	high core hardness-hot working dies	high core hardness-drawing dies, hot working dies

these steels nor in others which have been applied to any extent commercially; in fact, its presence in appreciable quantities has been considered, in most quarters, to be undesirable. Nickel has been blamed for "temper brittleness" and for opposing nitrogen absorption with resultant decrease in the case hardness obtained in nitriding.

Acceptance of these views to represent the effects of nickel in nitriding steels was, perhaps, to be expected since certain high nickel alloys such as Monel metal and the "stainless steels" (containing 25 per cent chromium and 20 per cent nickel) have served successfully as containers in nitriding furnaces[2, 3] where the requirements of resistance to ammonia catalyzation and nitrogen absorption are directly opposite to those of steels to be nitrided.

Several years ago studies were undertaken to determine what role nickel might play in nitriding steels and this paper contains a summary of some of the conclusions and a small part of the data obtained from extensive tests.

II. Advantages of Nitriding

Probably the principal technical advantages of the nitriding

[2]J. W. Harsch and J. Muller, "Nitriding Containers," *Metal Progress*, December, 1931, p. 41.

[3]O. E. Harder, "Nitriding for the Engineer," *Metals and Alloys*, September, 1931, p. 132.

process, comprising exposure of suitable metals to ammonia gas at temperatures under 1000 to 1100 degrees Fahr. (540 to 595 degrees Cent.), are (1) the procurement of appreciably higher hardness in the marginal layers of steel articles than that obtainable by other known methods of heat treatment, and (2) the procurement of this high hardness without the distortion encountered in martensitization (quenching).

The extent of the increases in case hardness which can be obtained when nitriding replaces carbon case hardening is shown in Fig. 1, reproduced from a paper by Sergeson.[4] Originally this in-

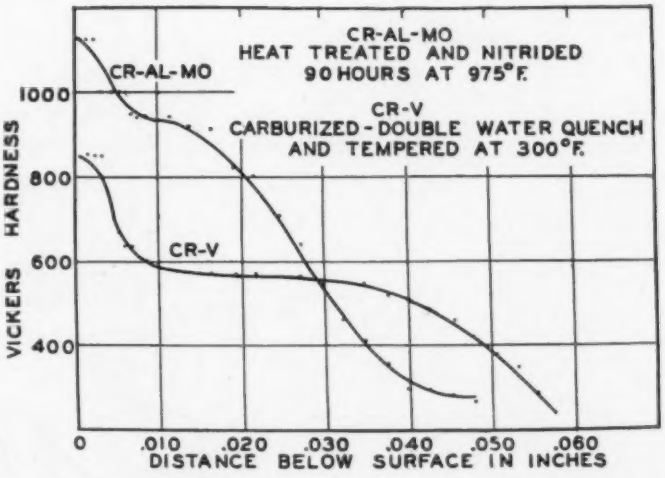

Fig. 1—Hardness and Penetration in Nitrided Cr-Al-Mo Steel (Nitralloy) and Carbon Case Hardened Cr-V Steel (SAE-6115) (After Sergeson).

crease in hardness was the focus of attraction to the nitrided steels, but high hardness, by itself, is a property of somewhat restricted interest and value. In the nitrided steels, high hardness proved to be associated with other desirable properties so that definite fields of usefulness for the nitriding process and the products produced have been established.

At least under certain conditions, nitrided steels show a high order of resistance to adhesion and abrasion as well as exceedingly high resistance to penetration and they can be operated in contact with a variety of materials without "galling" or the development of high frictional temperatures. In nitrided steels containing aluminum as the predominant alloying element there is the added advantage of

[4]Robert Sergeson, "Investigations in Nitriding," TRANSACTIONS, American Society for Steel Treating, Vol 16, 1929, p. 111.

good resistance to softening with increase in temperature and evidence is now available to show that under certain conditions the nitride case has good resistance to corrosion.[5]

These benefits, however, have not been secured in known nitriding steels without sacrifice in other and perhaps equally desirable properties, notably toughness and resistance to shock, and this has restricted the usefulness of nitrided articles, especially for applications where heavy loads are encountered. As a result, it is becoming evident that the maximum case hardness obtainable may be less desirable than somewhat lower hardness combined with improved toughness or resistance to shock.

An example of the limitations imposed by lack of toughness in nitrided articles is shown in Fig. 2. Due to improper preliminary heat treatment, the nitrided case of this camshaft spalled badly under the stresses to which it was subjected in service in a customary type of internal combustion engine. The correction of such weaknesses in the nitriding steels would, no doubt, extend their fields of usefulness.

III. Previous Investigations

There is little information in the technical literature by which to appraise the effects of nickel in nitriding steels, although a number of references can be cited in support of the comments already made. In the patents issued to Fry[6] it is stated that an extraordinarily high hardness is acquired by nitriding steel alloys which "contain 0.5 to 2 per cent aluminum and, either separately or in any desired combination, 0.5 to 4 per cent silicon, manganese, nickel, chromium, molybdenum, tungsten, vanadium, titanium or zirconium, and up to 0.6 per cent carbon."

Nickel is here classified in a second group with many other elements but it is now known that these metals are not interchangeable as might be inferred from the wording of the patent but have very definite and, in some cases, directly opposite effects to nickel upon the case formed in nitriding.

It is also known that aluminum is not essential to the production of high case hardness; in fact, there are already on the American market, as is shown in Table I, a number of steels which are sub-

[5] See foot note (2).

[6] United States Patents, Number 1,487,584 and 1,649,398.

Fig. 2—Spalling as a Result of Brittleness in the Case of Nitrided Steel. Portion of a Camshaft which Failed.

stantially free from aluminum and which acquire cases of high hardness when subjected to the usual nitriding treatments.

In the results of researches reported by Fry[7] the nickel steels used by him showed little or no increase in the hardness of the marginal layers after being given the customary ammonia treatment.

[7] A Fry, "Nitrogen in Iron, Steel and Special Steels," *Kruppsche Monatshefte*, September, 1923, p. 137.

These results are confirmed for a somewhat wider range of nickel contents by other investigators, including Guillet,[8] who also found that nickel additions to chromium-aluminum steels induced temper brittleness or so-called "Krupp Krankheit."

Guillet's conclusions as regards the reduction in impact values of the core of nitrided steels as the result of the prolonged heating for nitriding were that—(1) "Chromium-aluminum steels are relatively not susceptible to the Krupp sickness," (2) "The chromium-nickel-aluminum steels are very susceptible to the Krupp sickness," (3) "Chromium-aluminum-molybdenum steels with a low nickel content are not affected by Krupp sickness," (4) "Chromium-aluminum-nickel-molybdenum steels are slightly prone to the Krupp sickness while retaining satisfactory physical properties." These conclusions were not confirmed in the more recent studies of Homerberg and Walsted[9] who found that nickel did not increase the susceptibility of the chromium-aluminum steels to temper brittleness.

Sergeson[10] found that the addition of nickel with chromium and aluminum resulted in steels showing satisfactory surface hardness, whereas the addition of nickel with molybdenum and aluminum resulted in steels having only moderately high case hardness but deep penetration.

Jones[11] reported that the plain nickel steels containing up to 5 per cent of nickel did not harden appreciably in their marginal layers when heated in ammonia gas and that the addition of nickel to vanadium steels lowered the case hardness. However, when nickel was added to chromium steels its effect in lowering the hardness of the marginal layers was greatly reduced.

These citations refer to the hardness-penetration characteristics and to the impact properties of the core or those of the nitrided articles. Little or no attention has been given to the case toughness or to other properties which so often are of considerable importance in the practical applications of steels.

Other investigators have included nickel-containing steels in

[8]L. Guillet, "The Nitriding of Steels, *Le Genie Civil,* Vol. XCI, No. 3, p. 38, 60, 86.

[9]V. O. Homerberg and J. P. Walsted, "A Study of the Nitriding Process," TRANSACTIONS, American Society for Steel Treating, Vol. 16, 1929, p. 67.

[10]See foot note (3).

[11]The Iron and Steel Industry, Dec. 1930.

their tests[12] but no systematic researches have been made of the role of nickel in nitriding steels. Neither has there been available information permitting the balancing or adjusting of the alloying elements to provide effective control of the hardness-toughness relations in nitriding steels.

IV. Plan and Test Methods

The tests to be described were made under a plan of cooperation between the Department of Physical Metallurgy of the Massachusetts Institute of Technology and the Research Laboratory of the Development and Research Department of The International Nickel Company, Inc.

The majority of the steels studied were melted in small high frequency furnaces but many larger melts were also secured from steel manufacturers.

In the first part of the research program small tube furnaces were the only ones available for nitriding. These were not entirely satisfactory and practically all of the preliminary tests were later repeated on samples nitrided in Leeds and Northrup nitriding furnaces with fans for gas circulation. Later, a Hevi-Duty nitriding furnace became available and was used for the nitriding of the torsion test specimens and many other samples. In the more recent experiments use was again made of Leeds and Northrup nitriding furnaces.

This shifting from one type of furnace to another was the result of factors not entirely within the control of the investigators but it is considered to have served a useful purpose since it necessitated some duplication of work which provided for greater dependence upon the results obtained.

The absorption and diffusion of nitrogen in the customary nitriding process, when the steel is heated in ammonia, is affected by many variables, at least some of which are not readily amenable to control. In consequence, unusual results are sometimes obtained and it is perhaps not safe to depend entirely on single comparisons of two products. Largely on this account the plan of investigation was based upon the study of iron alloy systems and not upon the comparison of a miscellaneous group of steels. In this way information was secured upon the trend of effects produced by the different alloy ad-

[12]See, for example, foot note (2).

ditions and it was often possible to cross-check the results obtained in individual sets of tests.

The evaluation of the properties of nitrided steels is somewhat complex since articles of dual nature must be considered, i.e., articles in which the marginal layers are hard and the core relatively soft. Additional complications are encountered by reason of the high case hardnesses which extend only to comparatively shallow depths and which are above the ranges in which reliable measurements can be made with some of the older and most widely used hardness testers.

In general, the case hardness tests were made with a Monotron hardness tester on taper ground bars, but Vickers and diamond Rockwell readings were also obtained in the latter phases of the investigation. Rectangular bars about ½″x½″x4″ were nitrided in the selected manner and subsequently one face was ground and polished to tapers of either 0.010 or 0.015 inch per inch, depending on the length of the samples. Tests at intervals along the length of the taper bars provided data for hardness-depth curves and an estimate of case depths.

Case toughness was determined in a number of ways. Probably the most accurate method of comparison of the case properties was the torsion test. Its selection was not due to any special interest in the torsional properties, per se, but to the adaptability of this test to determinations of case properties. By removing metal to different depths after nitriding, the maximum fibre stress in subsequent torsion tests was brought to different areas of the case and in this manner it was possible to secure a good idea of the strength, ductility and toughness throughout the entire case, or at least those portions having high hardness.[13]

Bend tests were also made on many of the steels but these did not, in general, provide the degree of differentiation afforded by the torsion tests. Both the bend tests and torsion tests required somewhat larger amounts of metal than were available, especially in the preliminary phases of the investigation. With the large number of steels to be examined some less exact but more quickly made tests, applicable to small samples, seemed to be desirable. After experimenting with different methods, it was decided to make all of the preliminary studies of case toughness with the Brinell hardness tester.

The "Brinell toughness" test devised was simply to determine

[13]The torsion tests were made on an Olsen torsion testing machine on specimens with an 8-inch gage length ¼ inch in diameter.

the load on a 10-millimeter Brinell ball (in kilograms) required to crack the case. At least in steels having case hardness over about 500 Monotron-Brinell the first cracking of the case was clearly audible in a quiet room. In this test the higher the load required to crack the case the higher was the case toughness rating.

This test, which can be speedily and easily made on small samples, is susceptible to criticism from a number of points of view. The cracking loads are influenced by the case depth, by the character of the surface, by the hardness of the core and by other variables. However, in spite of these valid objections, the Brinell toughness test simulates in some degree the conditions frequently encountered in service and it proved to be useful in differentiating between cases having a high degree of toughness and those with a low order of toughness. Furthermore, the superiorities in case toughness shown in the Brinell toughness tests were confirmed by the results of the torsion tests.

Impact tests were made on a Charpy-type machine on specimens having 2-millimeter "keyhole" notches. In the tests of nitrided samples the specimens were notched before nitriding, whereas for all other conditions the specimens were notched subsequent to the final heat treatments.

V. Influence of Nickel on Nitriding Steels

In considering the effects of nickel in nitriding steels it is convenient to discuss separately its effects upon the core and the case, although the characteristics of the latter are, in certain respects, intimately related to those of the former.

1. Effects on the Core

Nickel strengthens and hardens the core of most of the currently used nitriding steels, (See Fig. 5) and so helps to provide better support to the very hard and comparatively brittle case when it is called upon to resist deformation. This support, which is considered to be essential in carburizing steels, in applications involving high pressures, would seem to be an even more necessary requirement with the relatively harder and more brittle nitride case, which otherwise tends to crack and spall under load.

The refining action of nickel on the pearlite frequently evident in complex nickel-containing steels as a marked sorbitizing effect, is

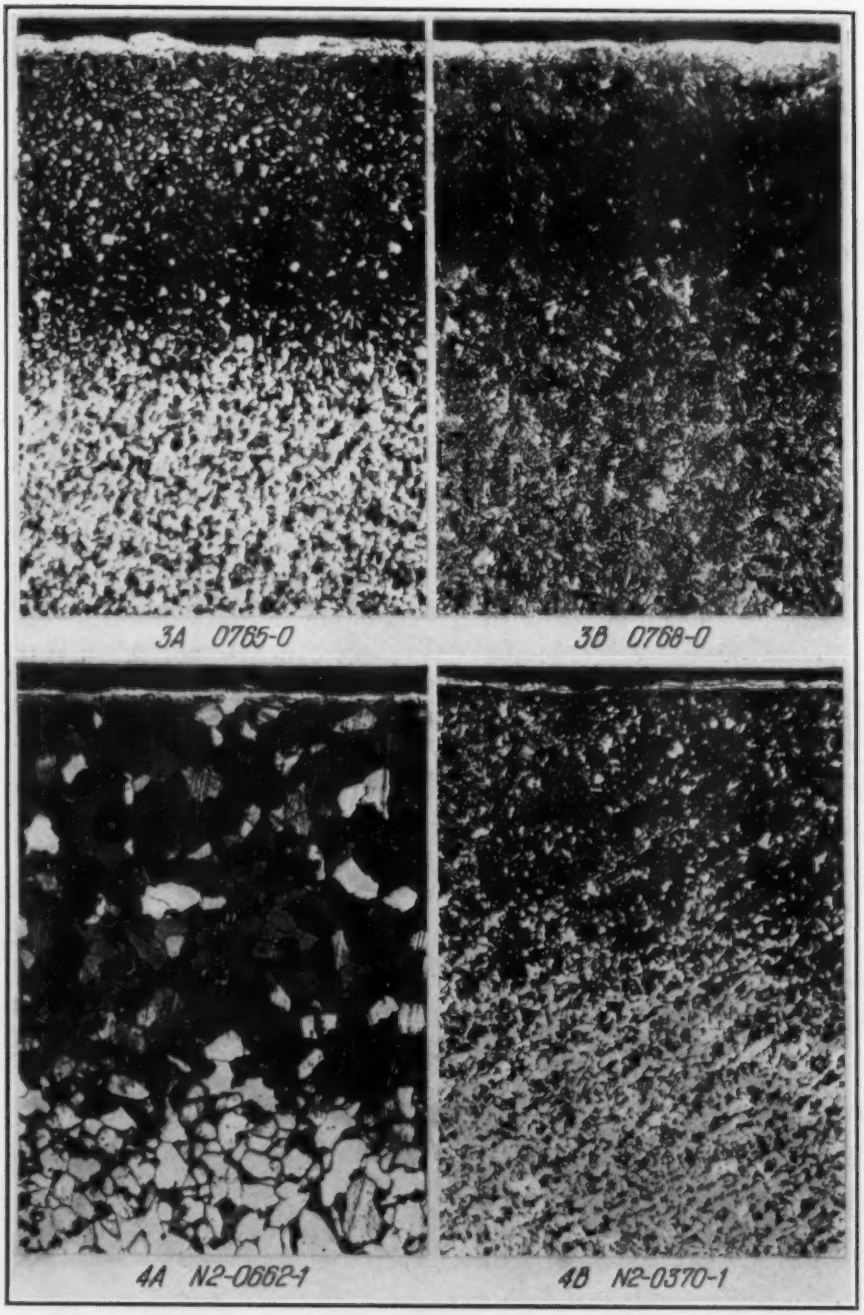

Fig. 3—Case and Core Structures of Normalized 1.1 Per Cent Chromium, 1 Per Cent Aluminum, 0.25 Per Cent Molybdenum Steels, With and Without Nickel. × 100.

3A. Without Nickel, Air-cooled from 1750 Degrees Fahr.

3B. With 3.6 Per Cent Nickel, Air-cooled from 1700 Degrees Fahr.

Fig. 4—Case and Core Structures of Normalized 0.75 Per Cent Chromium Steels With and Without Nickel. × 100.

4A. Without Nickel, Air-cooled from 1650 Degrees Fahr.

4B. With 3 Per Cent Nickel, Air-cooled from 1650 Degrees Fahr.

Steels Contain about 0.2 Per Cent Carbon, 0.5 Per Cent Manganese and 0.25 Per Cent Silicon. Samples Etched with 2 Per Cent Nitric Acid in Alcohol.

of value as regards both core and case and is illustrated in Fig. 3, showing a chromium-aluminum-molybdenum steel with and without nickel additions. Another example is shown in Fig. 4, where comparisons are given of normalized and nitrided samples of 0.7 per cent chromium steel with and without nickel. In both groups the nickel-containing steel has a finer structure and one which would be judged to show better mechanical properties than the corresponding steel without the nickel.

a. *Dispersion hardening phenomena*—In steels containing aluminum, the addition of nickel results in another important effect. In

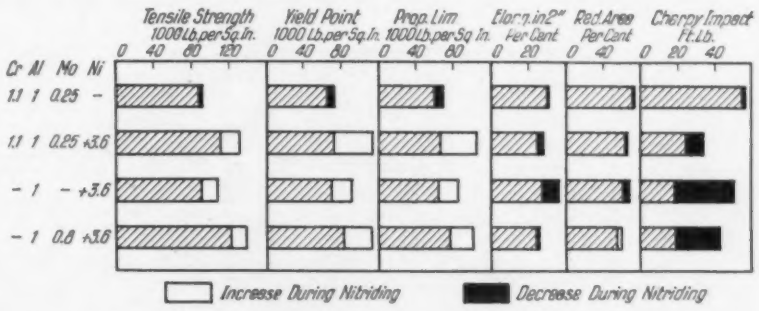
Tensile Strength 1000 Lb. per Sq. In.
Yield Point 1000 Lb. per Sq. In.
Prop. Lim 1000 Lb. per Sq. In.
Elong. in 2" Per Cent
Red. Area Per Cent
Charpy Impact Ft. Lb.
0 40 80 120
0 40 80
0 40 80
0 20
0 40
0 20 40
Cr Al Mo Ni
1.1 1 0.25 -
1.1 1 0.25 +3.6
- 1 - +3.6
- 1 0.8 +3.6
Increase During Nitriding
Decrease During Nitriding

Fig. 5—Core Properties of Different Nitriding Steels With and Without Nickel.

Comparison of Properties in Original Conditions (Quenched and Tempered before Nitriding) with Those After Nitriding. Shows the Results of Dispersion Hardening in the Steels Containing both Nickel and Aluminum.

the prolonged heating for nitriding at temperatures in the neighborhood of 975 degrees Fahr. (525 degrees Cent.) pronounced increases in hardness, strength and elastic properties are produced in the core, with decrease in the resistance to impact and moderate decreases in elongation and reduction of area in tensile tests.

In prior discussions of the changes in the core during the nitriding of steels containing nickel, the comments have most often been restricted to changes in impact resistance with the natural inference or definite suggestion that embrittlement was encountered and that this precluded useful applications of such steels.

This view does not appear to be adequate in evaluating the observed effects which have the characteristics of dispersion hardening phenomena. These effects have been observed in steels containing appreciable proportions of both aluminum and nickel[14] and the decreases in impact values of the core find compensation in increased

[14]Steels made in induction furnaces or by basic electric furnace practice—acid steel practice not considered.

core strength, higher elastic properties and increased hardness with the result that better support is given to the case when it is subjected to heavy pressures. These effects are illustrated in Fig. 5 and may be of decided advantage for some applications. But it is also important to recognize that the differences in impact values of the core, before and after dispersion hardening, are not necessarily representative of the differences in the nitrided steels, i.e., in the condition in which the nitrided articles are used.

This is especially important in small sections, such as those under test, where the embrittling effect of the hard nitride case completely overshadows the reduction in impact values of the core re-

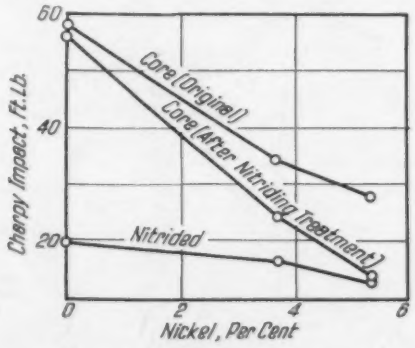

Fig. 6—Effect of Nickel on the Charpy Impact Values of the Core and of the Nitrided Specimens of 1.1 Per Cent Chromium, 1 Per Cent Aluminum, 0.25 Per Cent Molybdenum Steels.

Steels contain about 0.2 Per Cent Carbon, 0.5 Per Cent Manganese and 0.25 Per Cent Silicon. They were Water-Quenched from 1650 to 1700 Degrees Fahr. and Tempered 1½ Hours at 1300 Degrees Fahr. Before Nitriding 48 Hours at 975 Degrees Fahr. with About 30 Per Cent Ammonia Dissociation.

sulting from dispersion hardening phenomena. As is shown in Fig. 6, the nitrided chromium-aluminum-molybdenum steel, without nickel, showed a Charpy value of about 19 foot-pounds when nitrided for 48 hours at 975 degrees Fahr. (525 degrees Cent.). A similar steel with the addition of 3.5 per cent nickel showed 16 foot-pounds in the Charpy test under comparable conditions. The latter value is less than the former but it is of the same order of magnitude and the small difference between the two values does not reflect in any way the larger changes which occur in the core (55 and 34 foot-pounds respectively) as the result of dispersion hardening of the nickel steel.

In somewhat larger sections the core properties may be expected to be somewhat more important in determining the resistance to impact of the nitrided articles. But even under such conditions there is no evidence to indicate that the presence of both aluminum and nickel, and resulting dispersion hardening phenomena, are detrimental in the sense that losses in one direction do not find com-

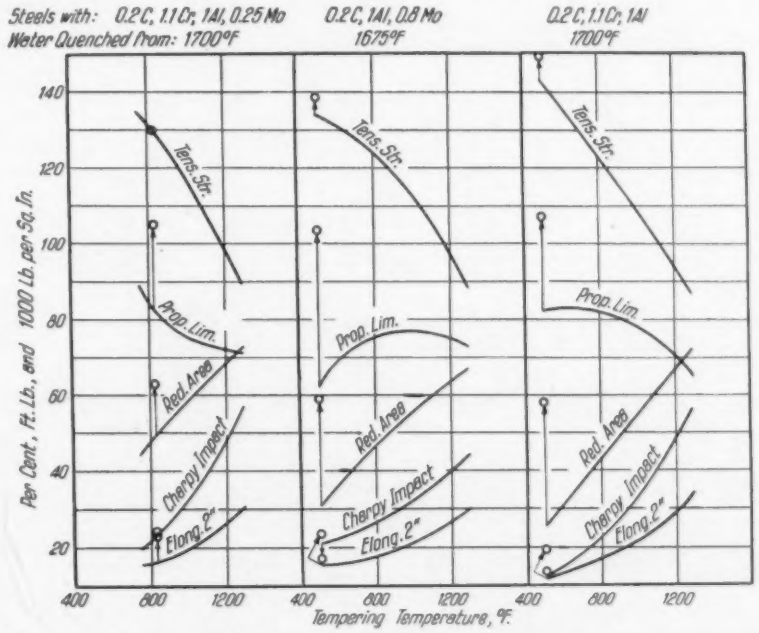

Fig. 7—Core Properties of Nitriding Steels, With and Without Nickel.

Curves Represent Steels Without Nickel Tempered at Different Temperatures.

Circles represent corresponding steels with 3.5 per cent added nickel, quenched and tempered at 1300 degrees Fahr. and then dispersion hardened in the nitriding cycle, 48 hours at 975 degrees Fahr. The circles are placed in the diagrams at tempering temperatures giving equivalent tensile strengths in the nickel-free steels.

See text for discussion.

pensation by gains in another. Actually the mechanical properties of the core may be considered to be improved, if both strength and ductility are given consideration. Evidence of this is shown in Fig. 7, where the nickel-containing steels, subjected to the nitriding heating cycle in air, are compared with nickel-free samples quenched and then tempered at lower temperatures to produce the same tensile strengths (without dispersion hardening). The dispersion hardened steels displayed higher elastic properties than were secured in the nickel-free steels by the lowered tempering temperature necessary to provide the same tensile strength. They also showed equally good or better ductility and resistance to impact.

There are obvious practical limitations to the core strengthening which can be produced in the nickel-free steels by lowering the tempering temperature in the preliminary heat treatment since stability of properties in the core will not be obtained unless the tempering is carried out at temperatures at or above the nitriding temperature (860-1050 degrees Fahr.) (460-565 degrees Cent.).

The foregoing comparisons were cited mainly to emphasize the point that the nickel alloy steel cores are not embrittled in nitriding

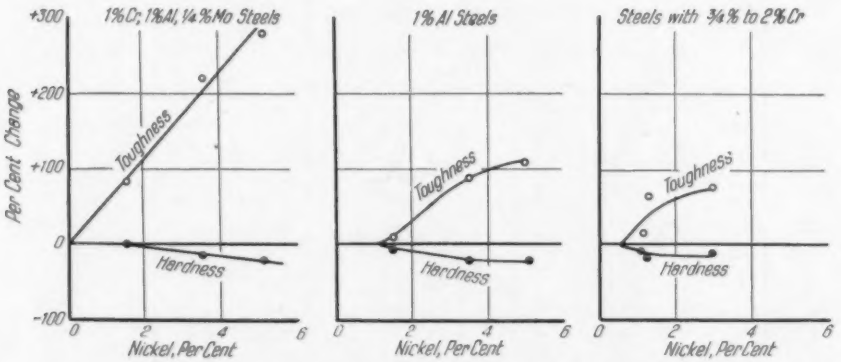

Fig. 8—Effect of Nickel on the Maximum Case Hardness and Case Toughness of Normalized and Nitrided Steels.

Hardness Determined by the Monotron Tester, Toughness by the Brinell Tester as Described in the Text.

Samples Nitrided 48 Hours at 975 Degrees Fahr. with about 30 Per Cent Ammonia Dissociation. Steels contain 0.10 to 0.30 Per Cent Carbon, 0.45 to 0.75 Per Cent Manganese, 0.20 to 0.30 Per Cent Silicon.

but merely show effects comparable to those observed under varying heat treatments of the nickel-free steels.

An important advantage of the dispersion hardenable nickel alloy nitriding steels is that they permit soft cores with relatively good machining properties to be transformed automatically during nitriding into stronger cores which are better able to support the case in service.

2. *Effects on the Case*

Nickel exerts a marked toughening effect upon the cases of nitrided steels with some loss in the maximum case hardness obtainable. The magnitude of these effects depends upon the compositions to which the nickel additions are made, the treatments, etc., but in general appreciable increases in toughness are obtained only with nickel additions of more than about 1.50 per cent, as is shown in Figs. 8 and 9. With increase in nickel to 5 per cent the case toughness increases rapidly and the maximum case hardness decreases.

Probably the most effective additions are between 2 and 3.50 per cent of nickel since in this range the decreases in maximum case hardness are of the order of only 5 to 12 per cent (Monotron-

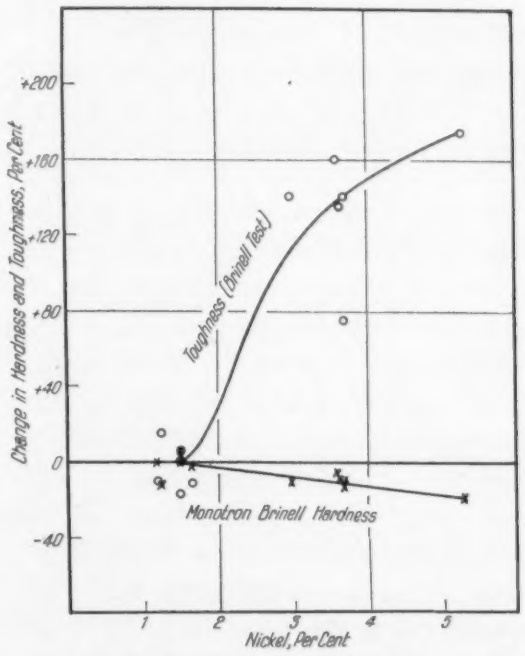

Fig. 9—Effect of Nickel on the Maximum Case Hardness and Case Toughness of Quenched and Tempered and Nitrided Steels.

Hardness Determined by the Monotron Tester, Toughness by the Brinell Tester as Described in the Text.

Samples Nitrided 48 Hours at 975 Degrees Fahr. with about 30 Per Cent Ammonia Dissociation.

The Steels Tested include 1.1 Per Cent Chromium-1 Per Cent Aluminum; 1.1 Per Cent Chromium-1 Per Cent Aluminum-0.25 Per Cent Molybdenum; 1 Per Cent Aluminum-0.8 Per Cent Molybdenum and 1.1 Per Cent Chromium-0.5 Per Cent Vanadium Steels, and more Complex Steels, with varying nickel contents, and about 0.10 to 0.30 Per Cent Carbon, 0.45 to 0.75 Per Cent Manganese, and 0.20 to 0.30 Per Cent Silicon.

Brinell) for steels which provide high case hardnesses, whereas the case toughness, as measured in the qualitative Brinell toughness test, previously described, increases to the order of 50 to 130 per cent.

VI. Use of Nickel in Nitriding Steels

The primary benefits from nickel additions to nitriding steels, as shown by the foregoing illustrations, are, therefore, found in one or more of the following:

(a) its strengthening and toughening effects upon the case with moderate decreases in case hardness
(b) its strengthening and hardening effects on the core by which to provide better support to the case
(c) its development of dispersion hardening phenomena in steels containing appreciable proportions of aluminum by means of which soft articles may automatically acquire higher core strength and elastic properties during nitriding.

High case hardness and concomitant properties are essentially the focus of attraction to the nitriding steels. Since nickel is primarily a case toughening element its effective use requires a knowledge of how to balance its effects with those of other elements which promote high case hardness. With such information it should be possible to provide improved case toughness at different case hardness levels, and the required core properties, to meet varied industrial requirements. For this reason, as well as to confirm the described effects of nickel over a wider range of compositions than those discussed, many alloy steel systems were studied. Space limitations will not permit detailed consideration to be given to all these tests but the compositions and properties of a few steels in which the beneficial effects of nickel are effectively utilized will be discussed briefly.

1. *Aluminum-chromium Steels with Different Nickel and Molybdenum Contents*

The 1 per cent aluminum, 1 per cent chromium steels, with or without molybdenum, are steels in which nickel can be used effectively in controlling and improving the case and core properties to meet varied service requirements. These steels have already been discussed in a general way but a correlation, and more nearly quantitative evaluation, of their properties should be useful.

As is shown in Fig. 10 increase in the nickel content up to about 5 per cent in the chromium-aluminum-molybdenum steels results in an appreciable and continuous increase in the torsional elastic properties of the case; it also results in increase in the torque required to crack the case and in the angular displacement before cracking will occur. These beneficial effects are observed in the zones of highest hardness and also at appreciable depths below the surface of the nitrided articles. They are supplemented, through dispersion

hardening phenomena, by large increases in the elastic properties, strength and hardness of the core with some decrease in ductility and impact resistance but, as was explained previously, these latter changes do not involve embrittlement in the usual sense of this term.

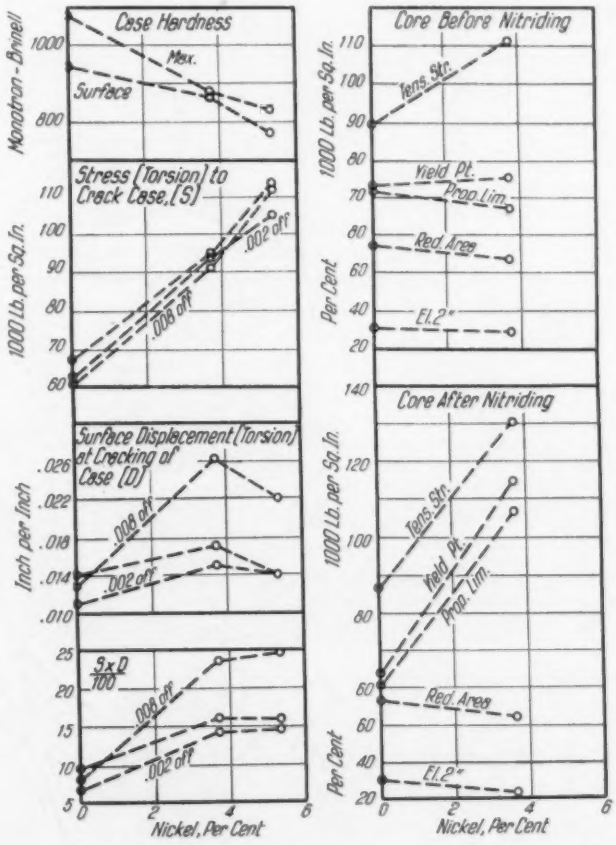

Fig. 10—Effect of Nickel on the Case and Core Properties of Quenched and Tempered and Nitrided Steels Containing About 1.1 Per Cent Chromium, 1 Per Cent Aluminum, 0.25 Per Cent Molybdenum, 0.2 Per Cent Carbon, 0.5 Per Cent Manganese, 0.25 Per Cent Silicon.

Steels Water-quenched from 1650 to 1700 Degrees Fahr., Tempered 1½ Hours at 1300 Degrees Fahr., Nitrided 48 hours at 975 Degrees Fahr. with about 30 Per Cent Ammonia Dissociation.

".002 off" Means that 0.002-inch of the case was Removed After Nitriding but Before Test.

With increase in the nickel content the case hardness decreases, somewhat slowly up to about 2.50 per cent of nickel but more rapidly thereafter.

Similar effects were observed in the chromium-aluminum steels which, in the presence of about 2 per cent or more of nickel, showed practically the same case properties as the corresponding chromium-

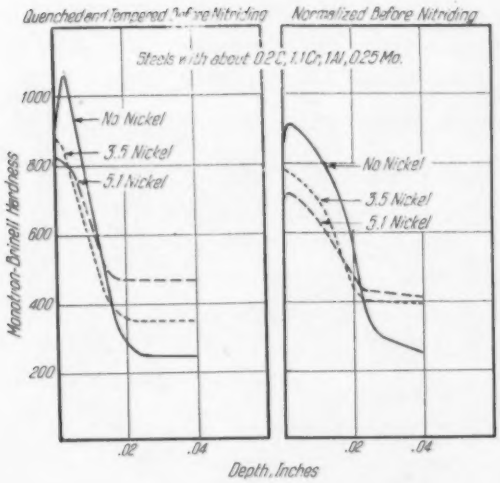

Fig. 11

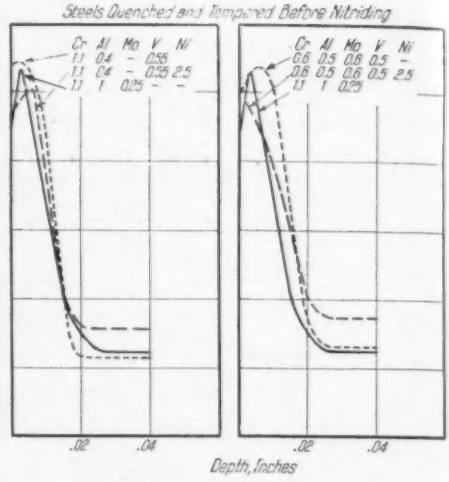

Fig. 12

Fig. 11—Hardness Penetration of Nitrided Chromium-Aluminum-Molybdenum Steels with Different Nickel Contents.

Steels Contain About 0.2 Per Cent Carbon, 0.5 Per Cent Manganese and 0.25 Per Cent Silicon; they were Water-quenched from 1650 to 1700 Degrees Fahr. and Tempered 1½ hours at 1300 Degrees Fahr., Nitrided 48 Hours at 975 Degrees Fahr. with about 30 Per Cent Ammonia Dissociation.

Fig. 12—Hardness Penetration of Nitrided Steels of Complex Composition.

Steels contain about 0.2 Per Cent Carbon, 0.5 Per Cent Manganese, 0.25 Per Cent Silicon; they were quenched from 1650 to 1700 Degrees Fahr., tempered 1½ hours at 1300 Degrees Fahr., nitrided 48 hours at 975 Degrees Fahr. with about 30 Per Cent ammonia dissociation. The Chromium-Aluminum-Vanadium and Chromium-Aluminum-Vanadium-Nickel steels were Quenched in oil, the Others in Water Before Tempering and Nitriding.

aluminum-molybdenum steels but with slightly lower core properties.

It is evident from Fig. 10 that the proportions of nickel to be added to the chromium-aluminum-molybdenum steels will depend upon the service requirements since a compromise is involved between improved case toughness and decreased case hardness. A steel with about 2.25 to 2.75 per cent of nickel would seem to be attractive for those numerous applications where improved case toughness and increased core strength must be secured with only moderate sacrifice in the case hardness. Such a steel may be made to the following specifications—

Carbon	To suit, between 0.10 to 0.40 per cent
Manganese	0.45 to 0.75 per cent
Aluminum	0.85 to 1.05 per cent
Chromium	1.00 to 1.30 per cent
Nickel	2.25 to 2.75 per cent
Molybdenum	0.15 to 0.25 per cent desirable but optional
Silicon, Phosphorus and Sulphur	Usual limits

It should show approximately the properties and the advantages

Table II

Approximate Case and Core Properties of Nitrided Cr-Al-Mo Steels With and Without Nickel

(Nitrided 48 hours at 975 degrees Fahr. with about 30 per cent ammonia dissociation)

	Nickel-containing Steel Per Cent	Customary Cr-Al-Mo Steel Per Cent
Type composition: Carbon	0.15	0.15
Chromium	1.10	1.10
Aluminum	0.95	0.95
Molybdenum	0.25	0.25
Nickel	2.50	...
	(by interpolation)	
Torsional properties of the case, as nitrided		
Proportional Limit, pounds per square inch	57,000	44,500
Stress to crack case, pounds per square inch	83,000	67,400
Surface displacement at cracking, inch per inch	0.016	0.014
Max. Case hardness, Monotron-Brinell	925 or more	1080
Depth of case in inches showing a hardness over		
800 Monotron-Brinell	0.008	0.008
400 Monotron-Brinell	0.015	0.015
Total case depth (based on hardness)	0.022	0.024
Tensile properties of the core, after nitriding		
Proportional Limit, pounds per square inch	93,000	60,000
Tensile Strength, pounds per square inch	115,000	86,300
Elongation in 2 inches, per cent	25	30
Reduction of Area, per cent	65	73
Charpy Impact, as nitrided, foot-pounds	18	19
Brinell Hardness, as quenched and tempered at 1300 degrees Fahr. before nitriding	185	165

over the customary chromium-aluminum-molybdenum steels, summarized in Table II.

For applications requiring greater case toughness and higher core strength than is given by this steel, and for which further decreases in case hardness may be acceptable, as for example in dies, larger nickel additions may be used effectively without changing the total case depth appreciably (Fig. 11). However, as the nickel is increased from about 2.50 to 5 per cent these steels become more strongly air hardening and they increase in hardness in the condition as quenched and tempered at high temperatures preparatory to nitriding. While machinable, the usual operations cannot be carried out as speedily on the higher nickel steels as on those with the lower nickel contents.

The examples cited have been given mainly to demonstrate the principle that by adding different proportions of nickel to the customary chromium-aluminum-molybdenum nitriding steels it is practicable to control the toughness-hardness relations of the nitride case and to provide better support to the case through stronger and harder cores. The range of properties obtainable are approximately those shown in Fig. 10 but it should be recognized that the quoted

Table III

Comparisons of Case and Core Properties of Different Nitriding Steels Containing Nickel

	Per Cent		Per Cent		Per Cent
Carbon	0.10	0.12	0.15	0.15	0.18
Chromium	1.10	1.10	0.59	0.62	1.17
Aluminum	0.42	0.40	0.49	0.44	0.95
Vanadium	0.58	0.55	0.56	0.55	...
Molybdenum	...	...	0.64	0.75	0.28
Nickel	2.45	...	2.44	...	...
Torsional properties of the case, as nitrided					
Proportional Limit, pounds per square inch	58,400	39,100	71,600	48,000	44,500
Stress to crack case, pounds per square inch	82,300	64,500	92,600	78,600	67,400
Surface displacement at cracking, inch per inch	0.009	0.009	0.010	0.009+	0.014
Maximum case hardness, Monotron-Brinell	1005	1085	975	1075	1080
Depth of case, in inches, showing a hardness over					
800 Monotron-Brinell	0.010	0.011	0.009	0.013	0.008
400 Monotron-Brinell	0.016	0.016	0.020	0.018	0.015
Total case depth (based on hardness)	0.020	0.019	0.024	0.023	0.024
Tensile properties of the core, after nitriding					
Proportional Limit, pounds per square inch	80,000		90,000		60,000
Tensile Strength, pounds per square inch	110,000		128,600		86,300
Elongation in 2 inches, per cent	23		20		30
Reduction of Area, per cent	70		60		73
Charpy Impact, as nitrided, foot-pounds	16	1.0*	18	15	19
Brinell Hardness, as quenched and tempered at 1300 degrees Fahr. before nitriding	310	230	345	260	165

*This value represents the average of two determinations but seems to the authors to be too low to represent the impact properties of the steel without nickel.

values are subject to modification depending upon the nitriding technique and the proportions of other elements present in the steel.

For example, increased case hardness can be secured by raising the chromium or aluminum contents, or both. However, the evidence now available indicates that increase in aluminum above about 1.10 per cent lowers the impact values of the nitrided samples appreciably unless other modifications in composition are made at the same time.

2. *Steels with Low Aluminum Contents*

The manufacture of steels with appreciable proportions of aluminum, of the order of 1 per cent or more, is not without disadvantages. Aluminum in such proportions adversely affects ingot and billet surfaces so that more conditioning is required than with most other commercial alloy steels. There is, therefore, an incentive for seeking nitriding steels with low aluminum contents, around 0.5 per cent, which can acquire hard and tough cases and which have desirable core properties.

A number of such steels are now known in which nickel plays an essential role and the compositions and properties of two of them are recorded in Table III along with those of the customary chromium-aluminum-molybdenum nitriding steel.

One of these steels contains about 1.10 per cent chromium, about 0.4 per cent aluminum, slightly more than 0.5 per cent vanadium and 2.50 per cent nickel. It may be viewed as a modification of the currently used chromium-vanadium nitriding steel (Nitralloy 630, Table I) in which the modifications comprise the addition of about 0.4 per cent of aluminum and 2.50 per cent of nickel.

This steel acquires a high case hardness on nitriding and the core is stronger and tougher than that of the chromium-aluminum-molybdenum steel. Its case depth (Fig. 12) and core properties are comparable to those of the latter steel and there are the added manufacturing advantages incident to the lower aluminum content.

It is shown in Table III that the chromium-aluminum-vanadium steel without nickel acquires a somewhat harder case than the one with nickel but it is weaker in both the case and core and the nitrided samples of the nickel-free steel showed low impact resistance.

Another nitriding steel with low aluminum content which shows interesting properties is one containing about one-half of one per cent of each of the four alloying elements, chromium, aluminum, molybdenum and vanadium together with about 2.50 per cent nickel. Its case and core properties and the beneficial effects of the nickel are also illustrated in Table III and Fig. 12.

In all of these steels nickel assumes the role of case strengthener and toughener; it hardens and strengthens the core directly and by dispersion hardening; and by varying the additions, nickel provides means for controlling the hardness-toughness relations of both the case and the core.

VII. General Discussion

The foregoing discussion has been simplified by citing data only for samples nitrided for 48 hours at 975 degrees Fahr. with an ammonia dissociation of about 30 per cent. This treatment is not to be considered the best suited for all purposes or all of the steels described but it is one which has been shown by many experiments to provide representative results. It will not necessarily give the maxi-

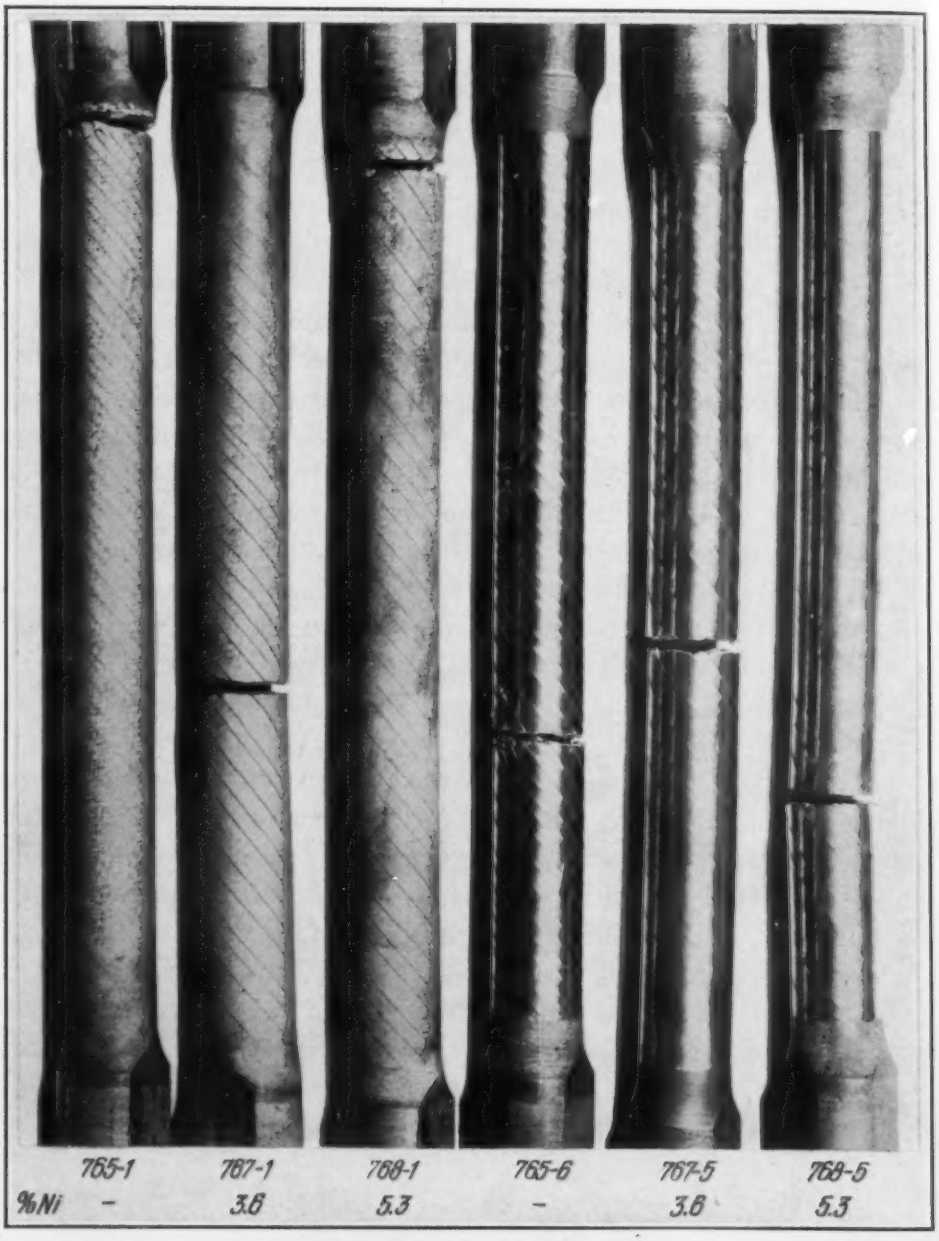

Fig. 13—Torsion Test Specimens of Nitrided Steels after Test, about ½ full size. The steels contain about 1.1 Per Cent Chromium, 1 Per Cent Aluminum, 0.25 Per Cent Molybdenum, 0.2 Per Cent Carbon, 0.5 Per Cent Manganese, 0.25 Per Cent Silicon.

The Three Specimens at the Left Were Tested as Nitrided; the Three on the Right had 0.016-inch removed from the Diameter after Nitriding but Before Test.

The Preliminary Treatment Comprised Water Quenching from 1650 to 1700 Degrees Fahr. followed by Tempering 1½ hours at 1300 Degrees Fahr. Samples were Nitrided 48 hours at 975 Degrees Fahr. with About 30 Per Cent Ammonia Dissociation.

mum case hardness but serves the present purpose of developing the role of nickel in nitriding steels.

Within limits, an increase in the nitriding time may be expected to provide increased case depth or increased case hardness or both. Sometimes an increase in the case hardness can be obtained by raising or lowering the nitriding temperatures, but such effects are pronounced only in those steels having a narrow nitriding temperature range and no evidence was obtained in extensive tests that any nickel-containing steels described in this paper fall into this classification.

It is now also agreed that more uniform results and better case toughness can generally be expected when the steels are sorbitized before nitriding than when ferrite envelopes surround lamellar pearlite. Accordingly, it is now customary to quench and temper nitriding steels, instead of normalizing, before nitriding.

The case toughening effects of nickel are evident upon nitriding quenched and tempered steels or normalized steels, but somewhat less nickel is required to produce appreciable benefits in the latter than in the former (compare Figs. 8 and 9). This is probably due to the sorbitizing effects of nickel, previously mentioned, and may be interpreted as an added advantage of the nickel steels for some applications where it is desirable to omit preliminary quenching operations.

The case toughening effects produced by nickel, which have been illustrated by the results of torsion tests and Brinell toughness tests on a variety of steels, are often clearly visible to the unaided eye as is evident from Fig. 13. Aside from the tension cracks shown in all of the torsion test specimens in the photograph a surface spalling will be observed in some of the samples not ground or polished after nitriding. This spalling is especially marked in the steel without nickel (765-1) and it decreases in intensity as the nickel content is increased.

This improvement in the outer layers of the nitride case was reflected in some cases also in a smaller difference in hardness between the surface and the underlying layers as is shown in the upper left hand corner of Fig. 10.

VIII. Summary

1. Typical data taken from extended studies of many alloy steel systems show that nickel may serve a useful role in nitriding steels. Its principal benefits are found in one or more of the following:

(a) its strengthening and toughening effects upon the case with moderate decreases in case hardness
(b) its strengthening and hardening effects on the core by which to provide better support to the case
(c) its development of dispersion hardening phenomena in steels containing appreciable proportions of aluminum by means of which articles may automatically acquire higher core strength and elastic properties during nitriding.

2. As the result of these effects, nickel may be added in varying and regulated proportions to suitable nitriding steels to control the toughness-hardness relations of the case and core and provide a wide range of properties to meet varied service requirements.

3. The effective use of nickel requires that it be balanced with certain other alloying elements. A number of low carbon nitriding steels are described in which the beneficial effects of nickel are realized; among these are the following types,—

(a) Steels containing about 1.1 per cent chromium
0.95 per cent aluminum
0.25 per cent molybdenum
0 to 5 per cent nickel
(b) Steels containing about 1.1 per cent chromium
0.4 per cent aluminum
0.5 per cent vanadium
2.5 per cent nickel
(c) Steels containing about 0.5 per cent chromium
0.5 per cent aluminum
0.5 per cent molybdenum
0.5 per cent vanadium
2.5 per cent nickel

The case and core properties of these new steels are described in detail.

Acknowledgments

The data in this paper were taken from researches extending over a period of several years. Acknowledgments are due to a number of the authors' associates who carried out most of the tests. Among these are Dr. J. P. Walsted, assistant professor of physical metallurgy, and Robert Bannon, instructor in physical metallurgy, Massachusetts Institute of Technology, J. W. Sands and Arthur Miller of the Research Laboratory, International Nickel Co., Inc.

DISCUSSION

Written Discussion: By Leon Guillet, director of the Ecole Centrale des Arts et Manufactures, Paris, France.

Since the initiation of the nitriding process, consideration has been given to nickel additions in steels containing chromium and aluminum to improve their mechanical properties. An appreciable improvement in the ultimate tensile strength and the elastic limit figures has been noted, but after nitriding the resiliency of the core is always greatly decreased, which phenomenon is attributed to temper brittleness. It was therefore natural to add some molybdenum, which element is known to have a favorable influence in avoiding such fragility. Actually, it has been noted that with up to 1.0 per cent of nickel, in the presence of 0.3 per cent molybdenum, the fragility of such steels is not increased during nitriding. For higher nickel contents the resiliency is diminished, although maintained within acceptable values. However, to date, nitriding steels containing nickel have been seldom used in France, although the decreased brittleness of the nitrided case in such steels has always been recognized.

Messrs. French and Homerberg have pointed out in a striking manner the favorable influence of nickel upon the strength of the core due to age-hardening during the nitriding process. The increase of the elastic limit and the tensile strength due to prolonged heating at about 500 degrees Cent. has not been sufficiently recognized to date, and to my knowledge, has not been profited by. This phenomenon is of great interest, permitting the ready machinability of pieces whose strength values are later increased during nitriding to such an extent that machining would have been extremely difficult or even impossible.

It seems to me that an addition of nickel in nitriding steels offers still another advantage, which is an increased penetration in quenching and the ability to readily heat treat pieces of larger dimensions. In France, self-hardening steels of the following approximate composition limits are employed in certain cases for nitriding steels:

	Per Cent
Carbon	0.20 to 0.40
Nickel	2.50 to 3.00
Chromium	2.50 to 3.00
Molybdenum	0.30 to 0.60
Aluminum	0.20 to 0.50

The carbon content varies in accordance with the application and the hardness desired after treatment. By varying the aluminum content, it is possible to regulate the hardness of the nitrided case, as well as the brittleness to some extent. After an air or oil quench and drawing at 500 degrees Cent., these steels have an ultimate tensile strength of from 150 to 160 kilograms per square millimeter (213,000 to 228,000 pounds per square inch), and a resiliency of 7 kilograms on a Mesnager test piece. Heating for 60 hours at 500 to 520 degrees Cent. lowers this resiliency figure by up to 25 per cent.

JEROME STRAUSS:[1] I wish to present some comments which are concerned chiefly with some of the methods used by the authors. They have employed what they described as a Brinell toughness test, mentioning objections to it which I do not think they should pass over so lightly, nor do I think they should attempt, after mentioning those objections, to use the test results quantitatively. The Vickers test with a very low load and much more shallow penetration, I believe should be more advantageous for measuring whatever they wish to describe as either toughness or ductility.

The torsion test seems to me to have very much more value. About seven or eight years ago I used it in a study of carburizing steels and carburizing methods, and it really does afford an excellent measure of combination of case toughness and adhesion to the core.

On page 494 it is shown that, as the core hardness is obviously greatly increased by the addition of 1.5 to 5 per cent nickel and the core hardness is important in the Brinell toughness test, the import of the toughness curves of Figs. 8 and 9 must be greatly different from that which is actually shown. This seems to be confirmed by the torsion tests which do not show increase in toughness due to the changes in composition that are nearly as large (in percentage increase over the value of the nickel-free steels). Furthermore, there is no measure of the increased toughness that may be due to the decreased hardness of the core, in some instances.

Then again, in Table III and also on page 493 at the end of the paragraph, it would have been very instructive and helpful in interpretation if there had been steels to show the influence of carbon as differing from the influence of nickel upon the properties that have been recorded.

Authors' Closure

Mr. Strauss has raised two questions in his discussion. In his first, he reiterates what will be found in the paper regarding the qualitative nature of the Brinell toughness test. Emphasis was placed on this but it is to be noted that the beneficial effects of nickel on the case properties of nitrided steels are shown both in the qualitative Brinell toughness tests and in the torsion tests.

With respect to the effect of carbon content, we cannot at the moment cite the numerical values involved but carbon increase will of course harden and strengthen the core. If the dispersion hardening produced in the nitriding cycle in steels containing both nickel and aluminum is superimposed on initially higher hardness provided by carbon increase, quite high core strengths or elastic properties can be obtained.

We should like to emphasize again that the theme embodied in the paper is not one advocating a single steel but a delineation of the role of nickel in nitriding steels. By suitable combinations of alloying elements, including nickel, a wide range of case and core properties can be secured to meet varied requirements.

We are greatly pleased at the interest shown in our findings by Dr. Guillet, who has also contributed additional information in his discussion of the paper.

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[1]Metallurgist, Vanadium Corporation of America, Bridgeville, Pa.

STRUCTURE ANALOGIES OF ALLOYS

By Arne Westgren

Abstract

Certain types of crystal structure have been found to recur frequently in the alloys of copper, silver and gold with metals such as zinc, cadmium, aluminum and tin. Especially the phases having the same structure as β-brass and γ-brass are of interest as they seem to be formed when the ratio of the number of the valency electrons to the number of the atoms assumes the values 3:2 and 21:13 respectively. In some cases, however, when according to this rule an alloy of β-brass structure may be expected, a phase isomorphous with β-manganese is formed instead (Ag_3Al, Au_3Al, Cu_5Si). When transition elements such as the iron, palladium and platinum metals are combined with zinc, cadmium or aluminum, phases analogous to β- or γ-brass are also formed. The rule stated above seems to apply also for them, provided the transition metals may be considered to have a valency of zero.

Chemical Characteristics of Alloy Phases

WHEN inspecting the surveys given in handbooks, such as the tabular work of Landolt-Börnstein, regarding the equilibrium diagrams of alloys, one is struck by the fact of how few analogies may be traced in the general aspect of the different diagrams. Only in a few rare cases, in which the systems are chemically closely related to each other, we are able to detect certain similarities. Thus, the diagrams of the copper-zinc, silver-zinc and silver-cadmium alloys resemble each other very much, a fact pointed out long ago by H. C. H. Carpenter. This author consequently also professed the phases of these systems to be built up in a similar way, an assumption which was also considered to be upheld by the close agreement in the microstructure of these alloys.

As such analogies in the aspect of equilibrium diagrams may be observed but rarely, it is natural that a simple comparison between the diagrams does not to any degree worth mentioning promote

The author, Dr. Arne Westgren, is professor of General and Inorganic Chemistry at the University of Stockholm, Stockholm, Sweden. Manuscript received June 13, 1931.

our knowledge regarding the question whether there does exist a more general relation between the different systems. For this purpose a closer investigation of the chemical character of alloy phases is required.

It is, however, not enough—as otherwise mostly in chemistry—to find out only the composition of the chemical individuals, which are present in the alloys, in order to characterize them. As we know, an alloy phase may often be homogeneous within a considerable concentration range, and it is difficult to decide whether a fundamental importance should be ascribed to a certain concentration value within this interval. Many phases—and as will be seen in the following the most important ones as regards the structural relationships—may not be defined adequately by means of their formulae derived through the common metallographic investigation expedients. It is therefore difficult to get a general survey of the great amount of data, obtained during the last decades as a result of metallographic research work, and which have been brought together in the equilibrium diagrams. A further treatment of this investigation material with the view of finding a relation between the different systems therefore cannot give any definite result until detailed investigations have been made concerning the character of the phases.

In X-ray methods metallography has of late found a new, valuable expedient for stating the characteristics of alloy phases. As we are now able to find out the crystal structure of the phases, the problem concerning the relationship between alloy systems may be attacked with greater prospects of success. This new expedient has to some extent contributed toward the solving of this problem, and a short survey of these results will be given in the following.

Structure Analogies in the Cu-Zn, Ag-Zn, Au-Zn and Ag-Cd Systems.—Fundamental Structure Types

X-ray analyses of the Cu-Zn, the Ag-Zn and the Au-Zn systems have shown that they are all built up in the same way. Every phase which occurs in the first system has its equivalent in the others. The concord is, however, not complete; in the Au-Zn system three phases have been found which have not been encountered in the others. Recently G. Natta and M. Freri have made an X-ray analysis of the Ag-Cd system, and, as might have been expected, they were able to prove that this system structurally resembles the Cu-Zn and the

Ag-Zn systems. Thus, Carpenter's assumption that the crystal structure of these three alloy series are analogous, has been corroborated.

At the same time as the work by Natta and Freri appeared, another X-ray analysis of the Ag-Cd system was completed at the Metallographic Institute of Stockholm. The results in the main agreed with those obtained by the Italian investigators. Some of the X-ray photograms taken hereby are given in Fig. 1. They have been taken according to the focussing principle, and contain only the most deviated interferences.

As may be seen, five phases appear in the Ag-Cd system at ordinary temperature. Their crystal structure is apparent from the unit cells, which have been drawn so as to correspond to the photogram series. After the face-centered cubic alpha phase follows the beta phase which possesses a cubic lattice with only two atoms in the elementary cube, and then comes the gamma phase which is body-centered cubic, having 52 atoms in the elementary cube, then the epsilon phase with a close-packed hexagonal structure, and finally the eta phase which has the structure of cadmium. The crystal structures of the three intermediary phases, appearing here, are of fundamental importance for the question regarding the structural relationship of alloys. As already stated they appear in the Cu-Zn, Ag-Zn and Au-Zn systems, whereby their homogeneity ranges in the different diagrams, given in atomic per cent, have approximately the same position on the concentration axis. This may be seen in Fig. 2. That the chemically closely related elements copper, silver and gold, alloyed with zinc or cadmium, form analogous structure series could naturally also have been anticipated. It is, on the other hand, much more surprising that these three structure types—or such which are closely related to them—occur in a great number of other alloys which differ widely in chemical respect from the systems mentioned.

Structure Analogies of the Binary Alloys of Cu, Ag and Au with Zn, Al, Sn and Sb.—Relation Between Structure and Concentration of Valency Electrons

During the study of gamma brass, we found that in the Cu-Al system a phase appears which is cubic and which holds 52 atoms per elementary cube. Later, a similar phase was detected also in the Cu-

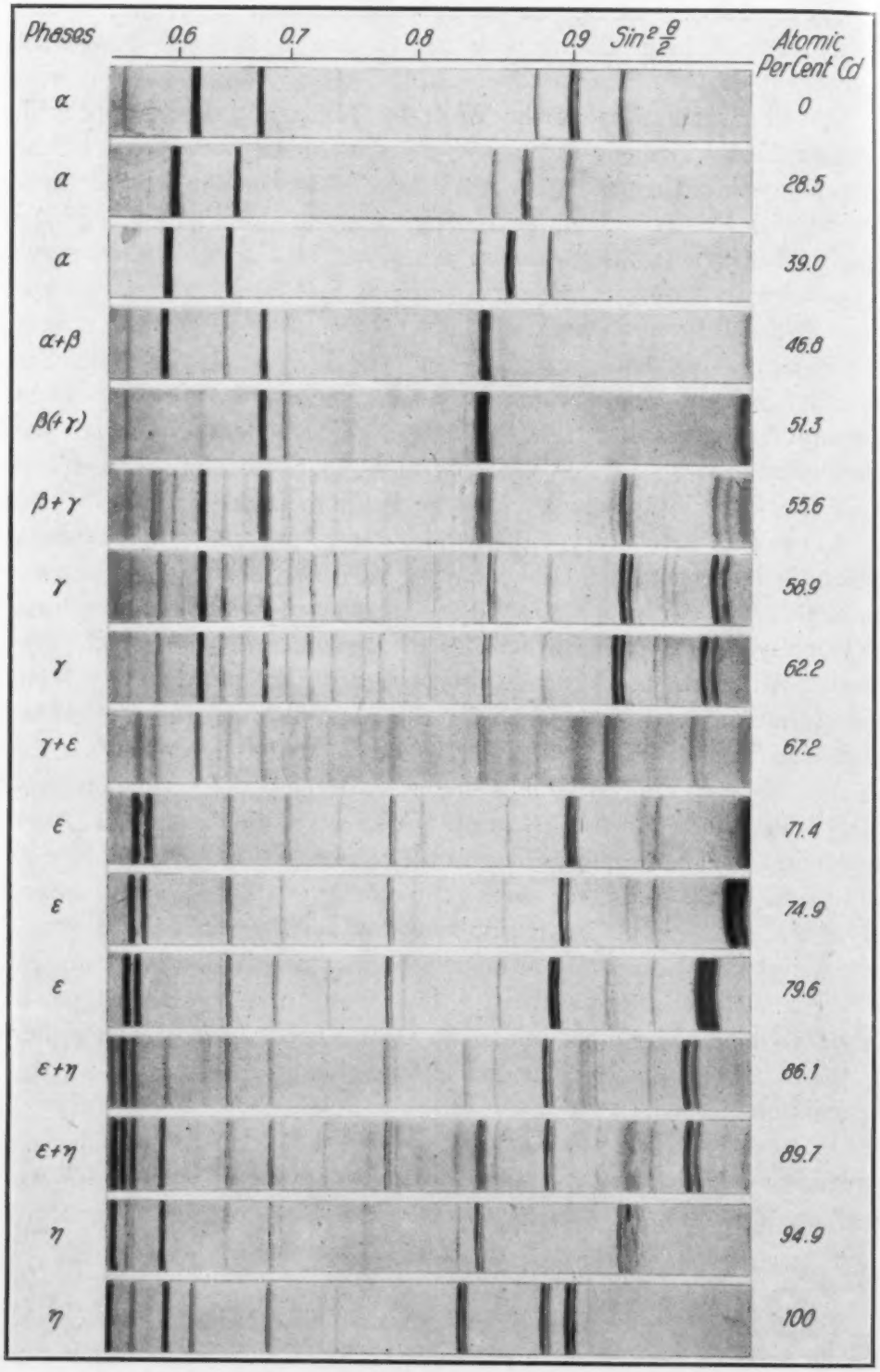

Fig. 1—Powder Photogram of Silver-Cadmium Alloys. Fe-*K* Radiation.

Sn system. In many alloys phases with close-packed hexagonal structure were encountered, and in the Cu-Al as well as in the Cu-Sn system we thought we had struck upon some phases analogous to

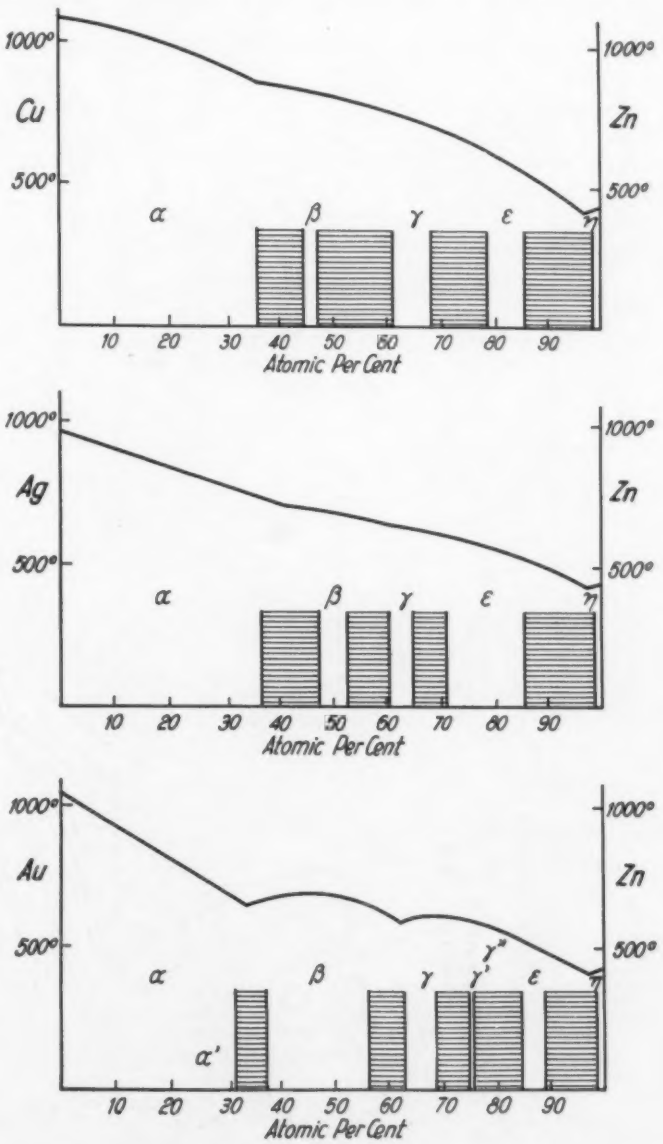

Fig. 2—Schematic Equilibrium Diagrams of the Systems Cu-Zn, Ag-Zn and Au-Zn.

those met with in beta brass. W. Hume-Rothery also from sundry reasons inferred that the beta phases of the Cu-Zn, the Cu-Al and the Cu-Sn alloys had the same structure, and based on the fact that the formulæ CuZn, Cu_3Al and Cu_5Sn could be ascribed to them

he raised the hypothesis that their structure is determined by the fact of an identical ratio of the number of valency electrons to the atom number (3:2).

A comparison was made on the same occasion between the complete diagrams of the three systems in question. It was found hereby

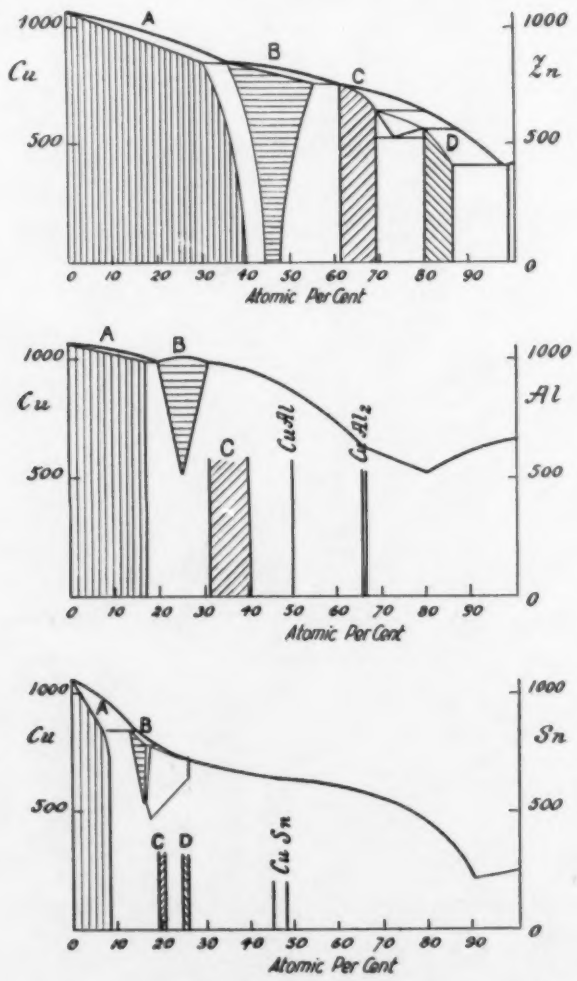

Fig. 3—Schematic Equilibrium Diagrams of the Systems Cu-Zn, Cu-Al and Cu-Sn.

that the homogeneity ranges of structurally analogous phases on increasing valency of the metal added to the copper are displaced toward the copper side, just as if the ratio of the number of valency electrons to the number of atoms were determinative of the formation of the lattice. A lattice type common for all the alloy series in all systems appears at a composition in which the valancy electron con-

centration assumes a value characteristic of this type—or at least very nearly approaches to the same (Fig. 3). This rule seemed to apply not only in the case of the copper alloys mentioned, but also in the Ag-Zn, Ag-Al and the Ag-Sn systems, in which intermediary

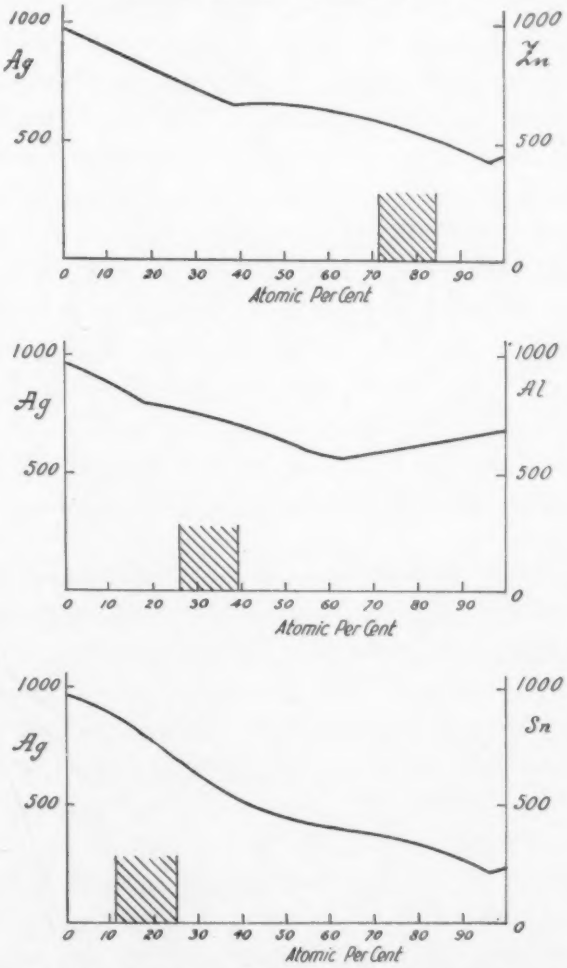

Fig. 4—The Approximate Homogeneity Range of the Close-packed Hexagonal Phase in the Systems Ag-Zn, Ag-Al and Ag-Sn.

hexagonal close-packed structures occur (Fig. 4). Since these observations were made an increased amount of investigation material on the scope in question has quickly accumulated. The hypothesis regarding the fundamental importance of the valency electron concentration for the formation of certain crystal species was upheld by orienting investigations of many alloys, carried out by V. M. Goldschmidt and his co-workers. X-ray analyses of metallic systems have also recently been made by other investigators, such as E. A. Owen

and G. D. Preston, L. Harang, C. H. Johansson and J. O. Linde, A. Sacklowski and others, and much work has been devoted to the same question in our Institute of Stockholm. A great number of phases have been detected, the structure of which may be referred to one of the three fundamental types mentioned.

In the following systems phases having the same structure as beta brass have been encountered: Ag-Mg, Ag-Zn, Ag-Cd, Au-Zn, Au-Cd, Cu-Pd, Cu-Al and Cu-Sn. Phases of this type possibly occur at higher temperatures in many other alloys, such as Ag-Al, Ag-Sb, Cu-Sb, and others.

Phases analogous with gamma brass appear in Ag-Zn, Au-Zn, Cu-Cd, Ag-Cd, Au-Cd, Cu-Hg, Ag-Hg, Cu-Al and Cu-Sn, and hexagonal close-packed phases have so far been found in the following alloys: Cu-Zn, Ag-Zn, Au-Zn, Ag-Cd, Ag-Al, Au-Al, Ag-In, Cu-Sn, Ag-Sn, Au-Sn, Cu-Sb and Ag-Sb.

Fundamental Values of the Valency Electron Concentration

The structure of gamma brass is exceedingly complicated. Despite this A. J. Bradley and J. Thewlis have succeeded in determining the atomic grouping completely. The 52 atoms in the elementary cube are apportioned into four groups of structurally equivalent atoms. These groups comprise the numbers 8, 12 and 24. Bradley and Thewlis were able to infer from photograms of the corresponding Ag-Zn and the Au-Zn phases in which the two atom species differ more as to diffraction power than is the case in the Cu-Zn alloys, that 8 + 12 atoms in the elementary cube consist of copper, silver or gold, the remaining 8 + 24 being zinc atoms. The formulae of the chemical compounds which correspond to these phases would consequently be Cu_5Zn_8, Ag_5Zn_8 and Au_5Zn_8. In analogy with this the corresponding crystal species of the Cu-Cd and the Au-Cd systems would be Cu_5Cd_8 and Ag_5Cd_8. Their homogeneity ranges, comprising only a few atomic per cent, also actually hold the concentration values which correspond to these formulae.

The corresponding Cu-Hg phase has, however, been reported to form an exception from this rule. According to N. Katoh there is in fact a phase present in copper amalgams which has the same structure as gamma brass, the different atomic species seem even to be distributed upon the lattice points to make the structure body-

centered as that of gamma brass, but it is reported to be homogeneous at about a mercury content as low as 45 atomic per cent. This statement can, however, hardly be accepted as definite, because it is difficult to obtain complete diffusion equilibria in copper amalgams. A comparison between the lattice dimensions of gamma Cu-Hg and those of the corresponding phases in the Cu-Cd, Ag-Cd and Ag-Hg systems will probably throw some light upon this question. For that purpose the silver amalgams must, however, be more thoroughly investigated than they have been to date.

As already mentioned, a phase likewise appears in the Cu-Al system which is cubic and which contains 52 atoms pro elementary cube. Judged by the first photograms taken it seemed close at hand to assume that the substitution of atoms with increasing aluminum concentration in this phase was not, as is generally the case, a simple one, but that instead three copper atoms were replaced by two aluminum atoms. The lattice dimensions appeared to decrease with increasing aluminum content within the homogeneity range in spite of the aluminum atoms being larger than the copper atoms. A closer investigation of this strange phenomenon by means of more accurate photograms has, however, recently shown that the circumstances are actually still more complicated than anticipated.

At one of the boundary limits of the homogeneity range the elementary cube contains 36 copper atoms and 16 aluminum atoms. Of these 36 copper atoms two may be substituted by aluminum atoms in a normal way, implying growth of the lattice. On still increased aluminum concentration most of the interference lines in the photograms split up, whereby a few, however, remain single and quite sharp (Fig. 5). In the photograms of the normal alloy, the latter corresponds to interferences, the three indices of which are the same, such as 222 or 444. Evidently, the symmetry falls from being cubic to a lower degree. On an increased aluminum content the distances between the lines of the multiplets become greater, and the displacement of all interference lines indicates a decrease in the lattice dimensions. The question whether this decrease in symmetry proceeds continuously must remain open. In order to solve this problem completely it is necessary that precision photograms of single crystals be taken.

The most important point in the present connection is the fact that the homogeneity range of the cubic phase embraces only the relatively narrow range $Cu_{36}Al_{16}$-$Cu_{34}Al_{18}$. The simplest composi-

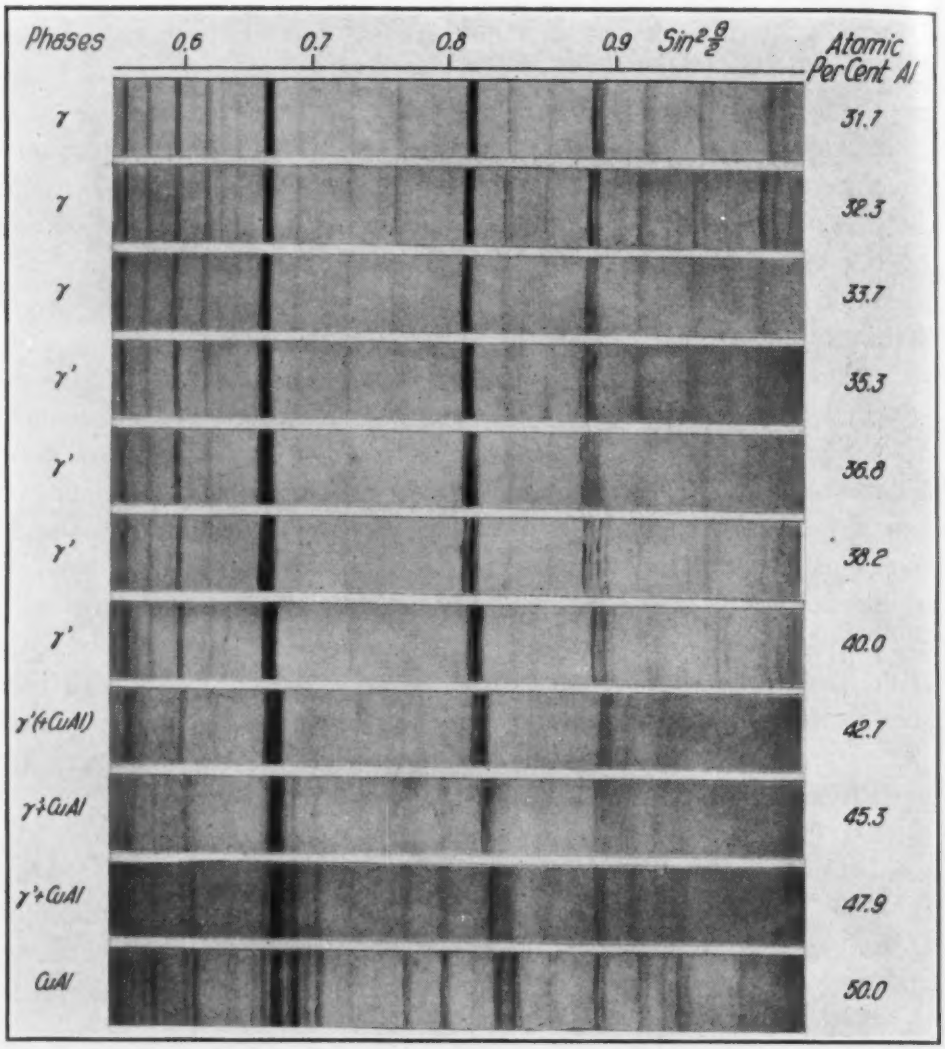

Fig. 5—Powder Photograms of Copper-Aluminum Alloys in the Range 31-50 Atomic Per Cent Aluminum. Fe-K Radiation.

tion, as regards formulae, within this range corresponds to Cu_9Al_4. According to a recent investigation of Bradley the two-atom species are here divided into groups of structurally equivalent building stones, in such a way that the composition corresponding to the formula Cu_9Al_4 may be considered as fundamental for this phase.

If this formula Cu_9Al_4 is compared to some one of the above-mentioned analogous phases, e. g., with Cu_5Zn_8, we will find that the sum of the valency electrons of the thirteen atoms will in both cases be 21, i. e., the fundamental ratio of the number of valency electrons to the number of atoms will in these phases be 21 :13.

If we wish to calculate which proportion should be used in the case of mixing a univalent metal, such as copper, with a tetravalent one, e. g., tin, in order to obtain the same valency electron concentration we will arrive at a composition indicated by formulae of the type $Cu_{31}Sn_8$. As a matter of fact, just at this concentration, and only there, i. e., at 32.6 per cent Sn the phase is homogeneous in the bronze system—which is analogous to gamma brass, and gamma Cu-Al. The series of Cu-Sn photograms, given in Fig. 6, shows that the homogeneity range of this phase is very narrow; its lines are not displaced when the homogeneity range is passed.

As we know, $Cu_{31}Sn_8$ differs from Cu_4Sn only by 0.8 per cent., and the phase in question is also often indicated by the latter more simple formula. Already the first investigators who made a detailed investigation of the Cu-Sn system, Heycock and Neville, and also Shepherd and Blough were actually able to state that a bronze with a composition corresponding to the formula Cu_4Sn is not homogeneous; the alloy becomes homogeneous only at a tin content about one per cent higher. The above reasoning has thus shown that the fundamental valency electron concentration of the complicatedly formed gamma phases of the Cu-Zn, Cu-Al and Cu-Sn systems is 21:13.

It should be pointed out, however, that the phases analogous to gamma brass are not quite identical in structure. When copper, silver or gold is alloyed with a bivalent metal (Zn, Cd, Hg) forming a gamma phase, its atomic grouping is body-centered cubic, whereas Cu_9Al_4 has a simple cubic lattice and $Cu_{31}Sn_8$ a face-centered cubic structure with 8 x 52, i. e., 416 atoms in its unit cell. The fundamental lattice seems to be the same in all these cases, only the distribution of the different kinds of atoms on the lattice points seems to be variable.

As already mentioned in the preceding the stability of the beta phases seems to be connected with the ratio 3:2 of valency electrons to atoms. In all analogous beta phases the points occupied by the atoms form a body-centered cubic lattice. The distribution of the two kinds of atoms upon the lattice points, however, varies according to their relative proportions.

If the phase is built by the two kinds of atoms in equal proportions, a so-called CsCl structure will arise, i. e., the lattice is formed by two simple cubic lattices, centering each other, each of which contains mainly atoms of the one kind (Fig. 7a). The formulae Cu-Zn, Ag-Zn, Ag-Hg, Ag-Cd, etc., may thus apply for these phases.

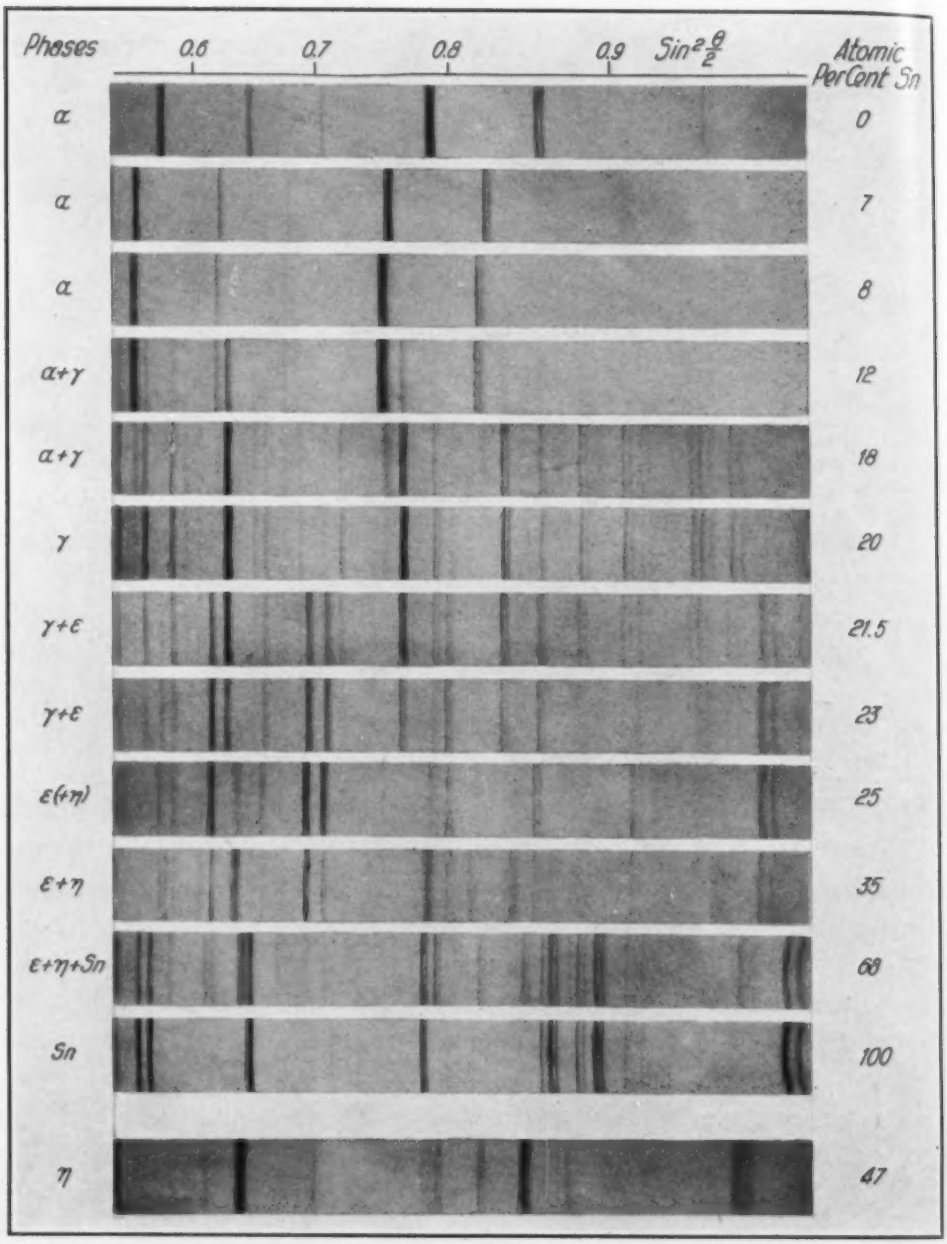

Fig. 6—Powder Photograms of Copper-Tin Alloys. Fe-*K* Radiation.

The lattice of the beta phase in the Cu-Al system is evidently face-centered. A space-centered cubic lattice may be viewed upon as having formed from four face-centered lattice with twice the parameter. In the copper phase only one of these four lattices holds mainly aluminum atoms, the other three containing copper atoms

(Fig. 7b). As stated recently by Elis Persson of the University of Stockholm this structure at least appears when approximately one-third of the copper atoms in the phase in question are substituted by manganese atoms, i.e., ranging amongst the alloys of the Heusler type. It therefore also seems probable that the same structure should apply even for the unsubstituted beta Cu-Al phases, and the formula Cu_3Al would consequently be valid here.

In the beta phase of the Cu-Sn system which by means of a severe quenching of the alloy can be fixed at ordinary temperature the two kinds of atoms are distributed at random on the points of

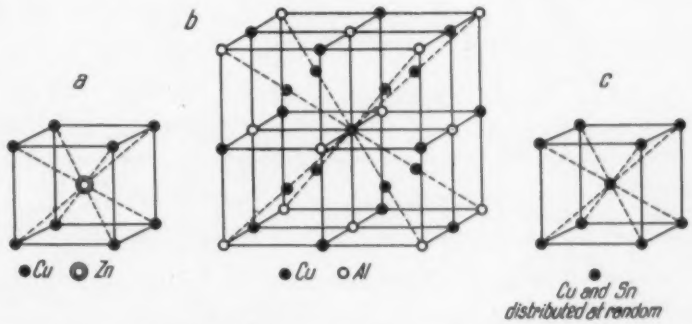

Fig. 7—Atomic Grouping of the β-Phases in the Systems Cu-Zn, Cu-Al and Cu-Sn.

the body-centered cubic lattice. From the formulae of the compounds of the Cu-Zn and the Cu_3Al type as well as from the circumstance that the homogeneity range of the last mentioned Cu-Sn phase is situated at a concentration value corresponding approximately to the formula Cu_5Sn we may with Hume-Rothery assume that the valency electron concentration 3:2 must be of fundamental importance for the formation of intermediary metallic phases of this kind of structure type.

No discussion of this kind can be made concerning the hexagonal close-packed phases, because in all of them the distribution of the two kinds of atoms seems to be of a statistical nature. In the Cu-Sn system the homogeneity range of this phase is restricted to quite a narrow interval, situated at a composition corresponding to the formula Cu_3Sn, and this has been taken as a sign that the fundamental valency electron concentration of phases of this kind is 7:4. It seems, however, hardly possible to uphold this conception, as the occurrence of close-packed hexagonal phases in fact does not seem to be regulated by the concentration of valency electrons to the same degree as the phases already discussed. Recent investigations have

shown that there are phases of this kind present in the Au-Cd, Au-Hg and Cu-Si alloys, which all come next to the face-centered cubic Au and Cu phases, thus having a concentration of valency electrons which is considerably lower than that of Cu_3Sn. In the Ag-Cd system the close-packed hexagonal atomic grouping even occurs within two different concentration ranges, one from 69 to 83 atomic per cent cadmium corresponding to brass, and another at about 50 atomic per cent cadmium in a temperature interval of 211-430 degrees Cent.[1]

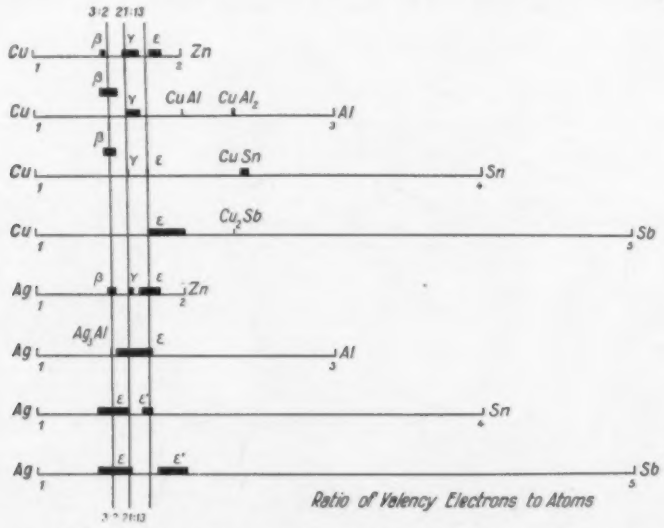

Fig. 8—The Homogeneity Ranges of Structurally Analogous Phases in Copper and Silver Alloys.

The concentration ranges of the phases of this kind present in the Ag-Sn and Ag-Sb alloys were at first believed to be rather extended. More detailed X-ray studies of these alloys have, however, revealed that they have a close-packed hexagonal structure only within part of these ranges. At compositions corresponding to Ag_3Sn and Ag_3Sb the structure is orthorhombic of a kind that might be considered to be derived from the close-packed hexagonal one by a slight distortion of the same.

In Fig. 8 is given a graphical survey of the structural relationship of the Cu and Ag alloys, being those which have been the most thoroughly investigated ones. In order to enlighten the comparison the homogeneity ranges of the phases in the different systems have been indicated on top of each other whereby one and the same scale

[1]Recent X-ray studies by A. Wolf on alloys of this composition performed as a continuation of a work by W. Fraenkel and A. Wolf, Zeitschr. f. anorg. u. allg. Chemie, Vol. 189, 1930, p. 145, have shown that they have the same structure as gamma brass both below 211 and above 430 degrees Cent. The same phenomenon is met with here as in iron.

of the valency electron concentration has been used. Hereby the phases which are stable only at higher temperatures have been marked down a little above the scale. The valency electron concentrations 3:2 and 21:13 have been indicated by straight lines. As may be seen, these lines almost without exception cut homogeneity ranges of analogous phases. It is only in the Cu-Zn system that one concentration range at ordinary temperature falls slightly at the side of the line, though not being very distant from the same. At an increased temperature the homogeneity range of the beta-Cu-Zn phase, however, grows so that it actually embraces the line corresponding to the valency electron concentration 3:2.

A vertical line has also been drawn corresponding to the ratio 7:4 of valency electrons to atoms. Although no stress may be laid upon this figure, it is seen however that the homogeneity ranges of the close-packed hexagonal phases of these systems include or fall in the vicinity of this line. This is valid for the Ag-Sn and Ag-Sb alloys only, however, only if we consider their pseudo hexagonal orthorhombic phases as belonging to the same group as the close-packed ones. Concerning this phase the approximative agreement in the concentration of valency electrons cannot, however, be considered to be of the same importance as in the case of the β-phase and γ-phase, because the homogeneity ranges are comparatively broad. In connection with the fact that in other copper, silver and gold alloys the close-packed hexagonal lattice type has been met with also at much lower concentration values than that indicated in the diagram this circumstance indicates that the concentration of valency electrons is an important but by no means the only factor which is determinative of the occurrence of a phase of this kind.

For the phases analogous to β- and γ-brass no exceptions save that of γ-Cu-Hg, which might be considered as somewhat doubtful, have been met with. The connection between structure type and the valency of the atoms indicates that in these cases the stability of the lattice primarily depends on the existence of a certain number of electrons, which seem in some way to belong to the lattice in its entirety. Only secondarily have the origin of these electrons or the properties of the atomic cores any influence on the atomic grouping. They seem to be of importance only for the formation of superstructures.

A new feature in these regularities of structural analogies has been discovered recently. Of the four elements in the series

vanadium, chromium, manganese and alpha iron, all but manganese are characterized by a body-centered cubic lattice. Manganese seems to be a unique element as regards its crystal structure; it crystallizes in two different forms, both of which are very complicated. The modification which is stable at ordinary temperature, alpha manganese, is cubic, having 58 atoms in its elementary cube, and beta manganese, stable at higher temperatures, is also cubic, but its

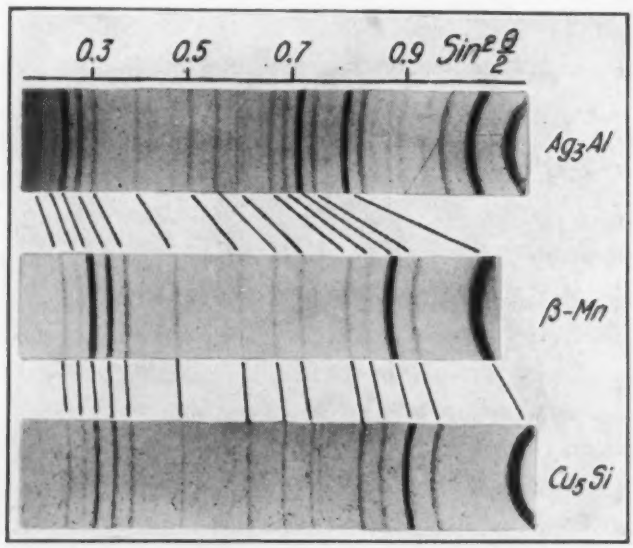

Fig. 9—Powder Photograms of Ag_3Al, β-Manganese and Cu_5Si.

elementary cube contains only 20 atoms. The latter modification is of special interest in connection with the crystal structure of certain compound metallic phases.

In some cases when in an alloy the ratio of valency electrons to atoms is 3:2 and a phase having a body-centered cubic lattice might thus have been expected, the atoms have instead been found to be grouped in the same way as in beta manganese. Just as this metal differs from its neighboring elements in respect to crystal structure, these intermetallic phases, for some reason, form exceptions from the general rule.

A phase of this kind is found in the Ag-Al system. Its range of homogeneity is so narrow that it may be denoted by a mere line in the equilibrium diagram. Its composition corresponds to Ag_3Al, from which it is evident that its ratio of valency electrons to atoms is 3:2.

Just recently at the University of Stockholm, by analyzing the

Cu-Si alloys Sven Arrhenius has met with a new representative of these peculiar phases of beta manganese structure. Its interference lines have just the same position, when it is in equilibrium with one or the other of its neighboring phases, from which it may be concluded that it also has a narrow range of homogeneity. It has not yet been chemically analyzed, but from the proportions of copper and silicon weighed together before the production of the alloy, as well as from a thermal analysis recently carried out by Matuyama, it is most probable that its composition corresponds to Cu_5Si. In this phase, too, the ratio of valency electrons to atoms seems thus to be exactly 3:2. The similarity of the photograms of beta manganese, Ag_3Al and Cu_5Si may be seen in Fig. 9.

Further cases of this kind will certainly be met with in the future, and it is to be hoped that we shall then have sufficient data, to enable us to understand why the one structure or the other presents itself, whenever the ratio of valency electrons to atoms is 3:2.

Structure Analogies of Alloys Containing Transition Elements in Combination with Aluminum, Zinc or Cadmium

Of late, several compound metallic phases have been found which do not contain copper, silver or gold, and yet have their atoms grouped in the same way as beta or gamma brass. Such a one is the phase NiAl, being built up of two simple cubic lattices centering each other, each of them being occupied mainly by atoms of one kind. From the close similarity between the equilibrium diagrams of the systems Ni-Al and Co-Al, it may be supposed that a phase of this kind is present also in the latter system. Investigations by E. Persson on the Cu-Mn-Al alloys have shown that, in this system, too, a phase is present which has beta brass structure, and which may be considered to be MnAl, with some of the manganese atoms replaced by copper atoms. Finally, at the University of Stockholm, A. Wolf has recently shown that in the iron-aluminum system the body-centered cubic phase of alpha iron has a homogeneity range extending from 0 to about 60 atomic per cent of aluminum. He has further found that a superstructure is formed in this phase, when it contains about 50 atomic per cent aluminum, which makes its atomic grouping for this composition analogous to that of NiAl and beta brass.

It is a common feature of all these phases that they are built up of aluminum atoms in conjunction with about the same number of atoms of a transition element.[2] If we assume that the rule of the ratio 3 valency electrons to 2 atoms, holding for the formation of beta brass structure in copper, silver and gold alloys, may be applied also in the cases of NiAl, MnAl and FeAl, it is an obvious conclusion

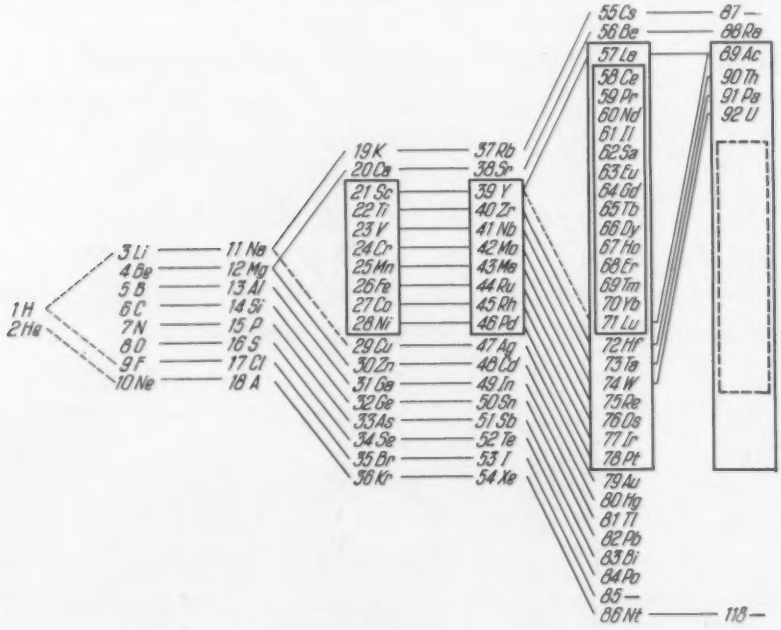

Fig. 10—The Periodic Table According to N. Bohr.

that in these phases the electrons belonging to the lattice in its entirety consist only of the valency electrons of the aluminum atoms. The atoms of the transition elements do not seem to contribute any of their electrons to those common to the lattice, but act as if they had a valency of zero.

The experimental data given above are, of course, too scanty to prove the correctness of this view, but, as we shall see in what follows, many other observations support it.

A. Osawa and Y. Ogawa have recently reported that there is a phase present in the iron-zinc system which has a gamma brass structure. It was previously supposed to be $FeZn_3$, but should, according to the Japanese investigators, be denoted by Fe_3Zn_{10} to fit in with the fact that there are 52 atoms in its unit cell.

A powder photogram of this phase is reproduced in Fig. 11. It

[2]Transition elements are those enclosed in frames in the periodic table of Bohr (Fig. 10).

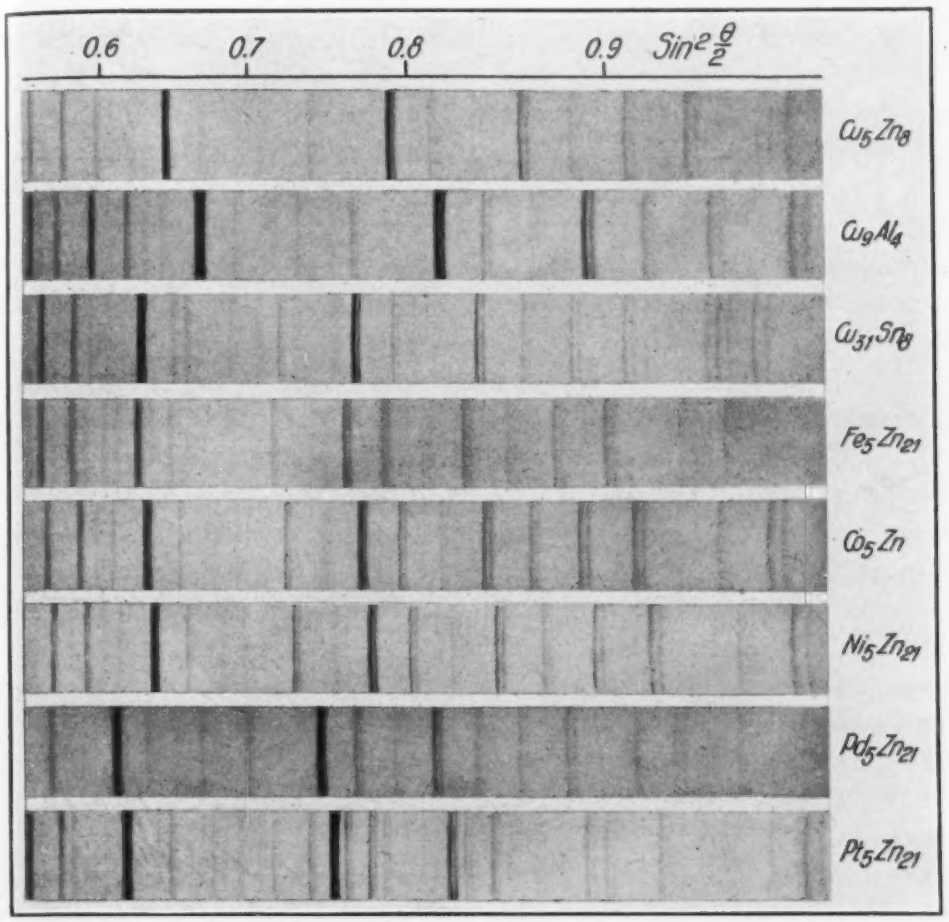

Fig. 11—Powder Photograms of Alloys Having γ-Brass Structure. Fe-*K* Radiation. Note: The fifth formulae from the top should be Co_5Zn_{21}.

is difficult to obtain true equilibria in the alloys containing this phase, so that an exact determination of its homogeneity range has not yet been obtained. From the fact that the lattice parameter changes from 8.962 Å to 8.992Å between its saturation limits, it may be concluded, however, that the homogeneity interval amounts to about 4 atomic per cent. Further, in the photograms of an alloy containing 28 atomic per cent iron, distinct alpha iron interferences may be seen in addition to those of the phase in question indicating that the latter has an iron content considerably lower than this concentration. It is most likely that the homogeneity range covers an interval of about 19 to 23 atomic per cent iron. The phase must not therefore necessarily be denoted by Fe_3Zn_{10} (with 23 atomic per cent iron), it may as well be considered to be Fe_5Zn_{21} (with 19 atomic per cent iron). If, in this case, iron is assumed to have a valency of zero, the latter

formula agrees with a ratio of 42:26, i. e., 21:13, of valency electrons to atoms. Thus support would again be given to the rule that a gamma brass structure is formed when the metals are combined in a proportion giving the said concentration of valency electrons.

To test whether this rule has a wider validity, W. Ekman of the University of Stockholm produced a series of alloys corresponding to the formula A_5B_{21}, where A is a transition element and B zinc or cadmium. The metals were melted together in evacuated, sealed quartz tubes, at a temperature of 900-1000 degrees Cent. (1650-1839 degrees Fahr.), and kept for about a week at this temperature.

In some cases this temperature was not high enough to produce a reaction between the metals (e. g., in the cases of Mo-Zn, W-Zn, Fe-Cd, Co-Cd), but when the alloying succeeded, the resulting product almost without exception turned out to be a homogeneous phase, of the expected gamma brass structure. In addition to the Fe-Zn alloy already mentioned, phases of this kind have so far been found in the systems Co-Zn, Ni-Zn, Rh-Zn, Pd-Zn, Pt-Zn, and Ni-Cd. In Fig. 11 some of the photograms of these alloys are compared to those of the analogous copper phases. Also in these alloys the lattice may be body-centered cubic (Co-Zn, Ni-Zn, Rh-Zn, Pd-Zn), simple cubic (Ni-Cd) or face-centered cubic with a parameter twice that of the other phases (Pt-Zn). The homogeneity ranges have so far been determined only for Co-Zn and Ni-Zn, and for them only approximately. The Co-Zn phase is homogeneous through an interval of about 15-22 atomic per cent cobalt and the Ni-Zn phase within about 15-19 atomic per cent nickel. When the nickel content exceeds the latter limit, the lattice is slightly deformed, which displays itself in a splitting up of most of its interference lines in the powder photograms. The same degradation of symmetry is evidently met with here as found previously in the analogous Cu-Al phase, when its aluminum content exceeds a certain level.

When the cobalt content of Co-Zn alloys rises above 22 atomic per cent, a series of lines appears in the photograms, indicating that a phase having the structure of beta manganese is formed. Its composition has not yet been determined definitely, but there are reasons to believe that it corresponds to $CoZn_3$. If, again, cobalt is assumed to have a valency of zero, this phase would thus have 3 valency electrons per 2 atoms and belong to the same group of intermetallic compounds as Ag_3Al and Cu_5Si mentioned above, which have a lattice of the beta manganese type.

It is a remarkable fact that the alloying of a transition element with aluminum, zinc or cadmium, is accompanied by a decrease in volume of the system much more pronounced than when alloys are formed only of atoms with complete inner electron shells. This contraction amounts, e. g., in the case of NiAl, to about 15 per cent, and according to Wolf, in the case of FeAl, to about 13 per cent. Although the phases corresponding to the formula A_5Zn_{21} contain but 19 atomic per cent of the transition element A, their formation is nevertheless accompanied by a contraction of about 5 per cent; in the case of Ni_5Cd_{21} it amounts even to 8.7 per cent. That the atoms of these alloys occupy a smaller space than usual, is possibly a phenomenon in some way connected with the fact that the transition elements in these cases act as if they had a valency of zero. A firmer binding of the electrons to the atoms may be expected to be accompanied by a decrease in atomic volume.

Additional Factors Influence the Lattice of Alloy Phases

It may be seen from the above that certain connections, easy to trace, actually do exist between the different alloy systems. Besides the mentioned, frequently occurring structures of the Cu-Zn system, others occur, which are common for many alloys, such as the fluorite and nickel arsenide structure. As observed by Goldschmidt phases of the last kind seem to be built up of atoms of transition elements in conjunction with elements having easily polarized atoms.

Thus, other factors than the number of valency electrons in the lattice can also be determinative of the formation of certain structure types. Very likely, the size of the atoms also plays an important rôle in this connection. That the valency electron concentration alone is not determinative of the formation of certain lattice types in alloys is evidenced by many facts. In the cases of the Cu, Ag and the Au alloys as well as the combinations of transition elements with aluminum, zinc and cadmium, the rule certainly applies, that the lattice types of beta and gamma brass appear only when the ratio of the number of valency electrons to the number of atoms assumes certain characteristic values, or approaches to them.

Vanadium, chromium, alpha iron, molybdenum, tungsten and many other elements may, on account of their body-centered cubic lattice, be considered to form structural analogies to beta brass. It may be regarded as doubtful, however, if their lattices really do con-

tain 3 valency electrons per 2 atoms. At all events, this can hardly be the case with the alkalin metals which have the same structure.

The rule of the approximately constant concentration of valency electrons for phases having beta brass structure is thus hardly applicable generally. How it may be for the so-called gamma phases must be left open, so long as no representative of this type has been found outside the groups of alloys treated above.

To this should also be added that in the systems where this rule does apply it is not reversible, i. e., even if the valency electron concentration assumes one of the above mentioned values the structure type which may be expected in many cases does not occur. Thus, no gamma phase is present in the Ag-Al system. In the Ag-Mg system a phase with gamma brass structure certainly occurs, but as found by B. Borén no other intermediary phase occurs, analogous to those present in the Cu-Zn alloys. The Cu-Mg alloys differ entirely from the Cu-Zn system inasmuch as a cubic phase Cu_2Mg, holding 24 atoms in the elementary cube and an orthorhombic phase, $CuMg_2$, occur, a circumstance pointed out by Anna Runqvist.

Even in the copper, silver and gold systems, in other respects following the uniform schedule mentioned, other phases than those discussed above occur. As indicated in Fig. 5 a phase CuAl and another one, $CuAl_2$ occur in the Cu-Al system. The first mentioned of these is orthorhombic and has a very complicated structure, the latter is tetragonal. S. Eriksson has found a tetragonal phase, Cu_2Sb, in the Cu-Sb system. It is analogous in structure to Fe_2Sb. In the bronze system occurs a phase CuSn, which has the structure of nickel arsenide, and in the interstices of which a number of copper atoms are distributed. It is analogous to FeSn, recently discovered by W. F. Ehret. The similarity between these copper alloy phases and the corresponding iron compounds indicates that copper in these cases exhibits its character of a transition element, which it may assume under certain conditions.

It is evident from the above that our knowledge is still very incomplete regarding the rules which govern the formation of compound metallic phases. Evidently, this problem is also a very complicated one. X-ray methods have contributed a little towards the solving of the question, and we have thus been able to raise a corner of the veil which has earlier covered this sphere of chemistry. We hope that continued X-ray crystallographic investigation of alloys will result in a still greater insight into these governing rules.

ALLOTROPY IN IRON AND STEEL

By R. H. Harrington and W. P. Wood

Abstract

The previous publication, by the present authors, concerning this subject is reviewed. Additional thermal analytical evidence is offered in support of the two-stage mechanism of allotropy originally suggested by the authors in their first paper. The recent results of other investigators are considered from this viewpoint. Recent work concerning the cause of lattice bonding, or structure, is reviewed. Several explanatory applications of a two-stage allotropic mechanism are offered.

Introduction

THE theory presented in this paper describes a possible mechanism for allotropy and represents a simple working conception that may be applied to many known facts. This theory must be supplemented with corollaries or supplanted with other theories as the future may reveal observed phenomena as a direct result of electronic configurations and atomic vibrations.

Manifestations of Allotropy and a Possible Mechanism

It becomes necessary to define allotropy according to observed facts as a temperature-critical change in lattice structure accompanied by abrupt variations in many physical and chemical properties. The definition obviously implies the various manifestations of an allotropic change as discoverable by thermal analysis; X-ray photography; microscopy; dilatometry; tensile, torsion, and compressive tests; magnetic and electrical measurements; chemical reactions; and other means.

In 1930 the authors (1)[1] presented data concerning the A_3 ranges,

[1]The figures appearing in parentheses pertain to the references appended to this paper.

A paper presented before the Fourteenth Annual Convention of the society held in Buffalo, October 3 to 7, 1932. Of the authors, who are members of the society, R. H. Harrington is research metallurgist, General Electric Co., Schenectady, N. Y. and W. P. Wood is professor in metallurgy, University of Michigan, Ann Arbor, Mich. Manuscript received August 2, 1932.

these data being derived from inverse rate heating and cooling curves obtained from a series of specially prepared iron-carbon alloys. It is pertinent at this point to consider some of the conclusions and interpretations made at that time.

1. Evidence was obtained that the A_3 change takes place in two stages. The first may be an energy change due to the change in such interatomic directional forces as determine the final lattice structure. The second may be a diffusion-like change as the atoms are moved from the positions in one lattice structure to those of another as in the change from gamma to alpha iron. The series of steels investigated gave consistent evidence of two energy changes for the A_3 transformation.

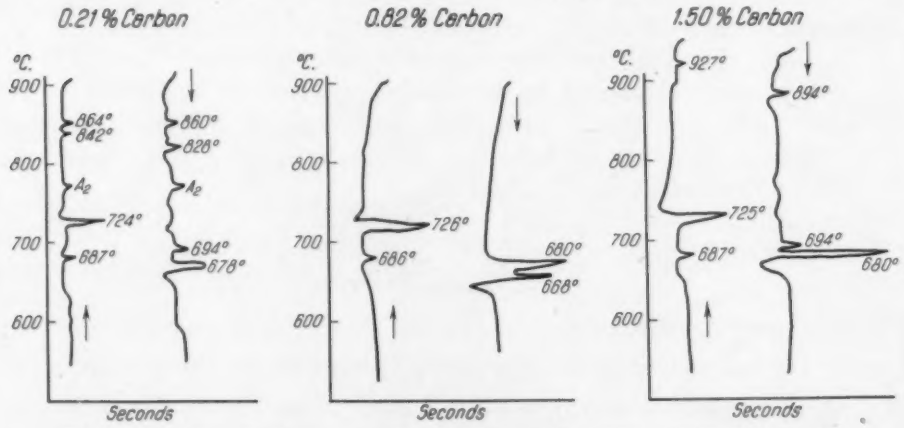

Fig. 1—Typical Heating and Cooling Curves for Three Different Steels.

2. The merging point of A_3 with A_2 occurred at about 0.60 per cent of carbon.

3. The slopes of the A_3 and A_{3-2} ranges seem to be about the same, which justifies drawing them in as a single straight line rather than a broken line.

4. The steel containing 0.82 per cent of carbon gave the best evidence of being the eutectoid alloy.

Following the publication of more recent work by other investigators it now becomes of value to consider the thermal analytical data concerning the A_1 changes in the special series of 32 steels.

Three typical curves are shown in Fig. 1 representing the hypoeutectoid steels (0.21 per cent carbon) the eutectoid steel (0.82 per cent carbon), and the hypereutectoid steels (1.50 per cent carbon). The heating curves for all of the steels containing more than 0.10 per cent carbon gave consistent evidence of two thermal arrests at

Table I

Heating and Cooling Curves of Steels Investigated

No. of Alloy	Per Cent of Carbon	Temp. ac_1	Temp. Ac_1	T° Diff. Ac_1-ac_1	Time ac_1	Time Ac_1	Temp. ar_1	Temp. Ar_1	T° Diff. ar_1-Ar_1	Time ar_1	Time Ar_1
1	0.00										
2	0.03	689	689	?	?	5?	689	689	?	?	7
3	0.04	695	695	?	?	5?	682	682	?	?	5
4	0.05	688	688	?	?	6?	686	674	12	5	7
5	0.07	689	689	?	?	5?	688	676	12	6	7
6	0.10	689	689	?	?	5?	686	674	12	4	11
7	0.15	688	726	38	7	10	682	682	0	..	10
8	0.16	687	730	43	5	13	688	680	8	8	14
9	0.20	687	740	53	6	12	685	685	0	..	18
10	0.21	687	724	37	5	15	694	678	16	6	15
11	0.27	687	720	33	5	15	686	670	16	5	15
12	0.37	687	725	38	5	10	683	683	0	..	18
13	0.39	687	725	38	6	20	696	680	16	8	22
14	0.40	687	722	35	6	20	683	683	0	..	23
15	0.43	687	722	35	6	18	682	682	0	..	20
16	0.44	687	726	39	6	18	694	683	11	7	18
17	0.45	687	722	35	6	20	694	682	12	5	18
18	0.52	688	726	38	7	22	683	683	0	..	30
19	0.59	688	727	39	7	27	684	674	10	34	32
20	0.61	688	727	39	7	28	683	683	0	..	50
21	0.64	684	726	42	8	36	687	687	0	..	52
22	0.66	684	728	44	8	26	684	684	0	..	54
23	0.74	684	725	41	6	28	685	670	15	28	24
24	0.77	686	726	40	8	32	682	670	12	68	24
25	0.82	686	726	40	8	30	680	668	12	30	18
26	0.90	683	726	43	6	36	686	670	16	60	34
27	0.99	686	723	37	6	24	687	687	0	..	70
28	1.11	683	726	43	6	22	688	670	18	32	14
29	1.13	683	725	42	6	34	687	687	0	..	60
30	1.21	686	726	40	8	34	690	690	0	..	60
31	1.48	685	725	40	7	28	687	687	0	..	42
32	1.50	687	725	38	8	28	694	680	14	7	56

Ac_1, a small one of the same degree as the A_3 change followed at a higher temperature by a larger one varying in intensity with the carbon content. Sixteen of the thirty-one carbon-containing alloys gave evidence of two thermal arrests at Ar_1, generally a small change followed at a lower temperature by a larger evolution depending upon the carbon content. Most of the thermal analytical work has resulted in more consistent observations of the A_1 changes from heating curves and of the A_3 changes from cooling curves. For the purpose of brevity the results of the heating and cooling curves are given in Table I.

It will be noted that the first thermal change upon heating starts consistently at 686 ± 3 degrees Cent. (1267 degrees Fahr.) and that the second and larger one occurs about 725 degrees Cent. (1337 degrees Fahr.) where the cementite solution is normally observed upon heating. The first arrest is a small one, of the degree of the one at A_3 and its length of time tends to increase slightly with carbon content. This may be accounted for by the mass effect on

hysteresis caused by an increase with carbon content of the amount of alpha iron that changes to gamma iron at Ac_1. The time deviation for the larger effect at Ac_1 increases greatly with carbon content. Inconsistencies in this tendency are accounted for by the broadening of the temperature range over which the solution reaction takes place. The narrower this range, the greater is the amount of time required at constant temperature to effect the change.

Upon cooling the reverse occurs. The first arrest at Ar_1 tends to be a small one of the same degree as that observed at A_3. In those steels in which it occurs the temperature interval is relatively small before cementite precipitation takes place. This is to be expected for as soon as the interatomic linkage becomes that of alpha iron, carbon must be precipitated as iron carbide. This very principle has actually caused the two reactions to be so nearly simultaneous that half of the series of steels shows but a single large thermal arrest. The second arrest in the cooling curve tends to increase in time deviation with those exceptions when the reaction takes place over a broader temperature range or where some of the carbide appears to precipitate simultaneously with the first step in the change from gamma to alpha iron. In both heating and cooling curves the second, or lattice shift, change is masked by, and is probably simultaneous with the carbide effect.

Upon heating, then, the interatomic directional forces shift from the alpha to the gamma type at 686 degrees Cent. (1267 degrees Fahr.). Cementite, as such, is stable at higher temperatures, as in hypereutectoid steels, unless there be gamma iron to dissolve it. Also mobility is greater at the higher temperature. It may even be the shift in atomic lattice, lagging behind the force direction change, initiates the carbide solution simultaneously at 725 degrees Cent. (1337 degrees Fahr.). Upon cooling, so long as gamma iron persists, the carbide remains in solution. However, as soon as the force links (or as the atomic law postulates) become those of alpha iron the solubility for the carbon is denied and, probably intensified by cooling hysteresis, the carbide is immediately, or almost immediately, caused to form. The time and temperature relationships of these reactions may have much to do in determining whether the carbide will form plates or spheroids.

There is, then, some evidence that the atomic shift in lattice may lag behind the change in lattice directional forces upon heating and cooling a steel under conditions other than those of absolute equi-

librium. If this is true, various observed data may show apparently anomalous facts such as lattices other than those of normal alpha and gamma irons in quenched steels. It becomes pertinent, then, to consider some of the recent data obtained by other investigators.

In 1930 Kurdoumoff and Evensen (2) found the following main structures in steels quenched with different cooling velocities and possessing a greater than expected hardness: 1. Tetragonal lattice having a definite axial ratio for a given carbon content; 2. Non-uniform tetragonal lattice; 3. A cubic lattice. Samples with one end quenched in water and the other cooled in air checked this observation by having three merging structure zones with characteristic etching rates and micostructures. X-ray examination showed that there were austenitic lines in the first (or water-quenched) zone and that the lattice was tetragonal. Austenitic lines were observed also in the second zone (just at water's edge). These lines were shifted in different directions with respect to the alpha lines. This shift gradually decreased with the approach toward the third (air-cooled) zone. There the alpha iron lines were superimposed upon the wide martensitic lines. In the third zone were the lines of alpha iron and Fe_3C. It was stated that the tetragonal structure represents the solid solution in which the iron atoms are arranged in the body-centered and greatly distorted tetragonal lattice, the carbon atoms being arranged between the iron atoms. The transformation of tetragonal lattice to cubic is accomplished by means of a gradual decrease in axial ratios.

Also in 1930 Dehlinger and Graf (3) published some observations on the 50 atomic per cent copper and 50 atomic per cent gold alloy. From X-ray diagrams of this copper-gold alloy the conclusion is drawn that the transition of the modification consisting of cubic solid solution to the tetragonal system passes through a well defined intermediate phase of definite lattice constant and tetragonal symmetry, though the atoms are only partly ordered. The electric conductivity is found to go parallel to the structural change. Though the cubic and tetragonal modifications are very soft, the intermediate state is exceedingly hard. The cause for the transition of the cubic phase to the tetragonal intermediate state must be due to the valency electrons.

In 1931 an article by G. Sachs (4) was translated and presented by Dr. S. L. Hoyt before the American Institute of Mining and Metallurgical Engineers convention in February 1932. X-ray evi-

dence from copper-silver, copper-aluminum, and gold-copper alloys leads to the conclusion that the mechanism of a transformation in an alloy can be considered as composed of two processes: 1. A rearrangement of the crystal symmetry, and 2. A change in the atomic arrangement. In quenched carbon steel there is a body-centered tetragonal structure which is assumed to be an unstable intermediate form in the transformation from face-centered austenite to body-centered alpha iron. The lattice change is practically complete but the carbon, as yet, has failed to precipitate out. Here again the rearrangement of the atoms is more sluggish than the change in crystal form. The tetragonal phase has been shown by examination of a quenched austenite crystal to be oriented in a fixed manner with reference to the parent austenite crystal. This is in line with the discontinuous character of the transformation and the fact that it is strongly affected by external forces. If the tetragonal lattice is tempered at temperatures of 100 degrees Cent., and above, it changes gradually into the stable body-centered cubic lattice of alpha iron. This can occur only with the precipitation of carbon out of the lattice, even though the existence of carbon or Fe_3C cannot yet be shown. Further, it could be shown that this reaction is fairly sudden and that intermediate concentrations (of carbon in alpha iron) exist only to a minor degree. The two step transformation is further justified by the author's kinetic derivations.

Arne Westgren (5) in 1931 showed by X-ray analyses that eutectoid steel, when normally quenched, consists of a slight quantity of austenite mixed with a solid solution of carbon in alpha iron, the lattice of which is distorted into a tetragonal shape by carbon atoms. Tempering at 150 degrees Cent. (302 degrees Fahr.) results in transformation into carbon-free alpha iron with extremely fine cementite.

The amounts of austenite, body-centered tetragonal martensite, and body-centered cubic martensite were determined in work (6) reported from the Tohoku Imperial University in 1931. X-ray studies were made of a 1.1 per cent carbon steel, water-quenched from 900 degrees Cent. (1650 degrees Fahr.) and drawn at successively higher temperatures. The results are given in Table II.

In 1932 Dehlinger (7) published certain principles and conclusions concerning phase changes. Some of these are as follows: 1. All X-ray studies of single crystals have shown that transformations take place within the single grain, at least partially, in one

Table II

Temperature of Draw Degrees Cent.	Per Cent Austenite	Per Cent Tetragonal Martensite	Per Cent Cubic Martensite
As quenched	31.2	69	Balance—0
55	30.7	69	
80	30.0	61	
100	28.8	54	
140	31.2	8	
170	23.2	0	
225	21.6	0	
235	14.9	0	
250	0	0	100

phase; that is, the original phase does not suddenly decompose but gradually transforms into one of the end phases, which is then crystallographically oriented toward the original phase. 2. Almost all transformations are accompanied by diffusion-like movements of the atoms. The velocities of these diffusions are retarded or increased by the free energy of the lattice changes which take place. 3. The relationship of diffusion-like processes and lattice changes is not simply established in metallic transformations. The relation of these two processes can vary with cooling rates and grain sizes. 4. In most cases the lattice change takes place considerably faster than the diffusion processes. This produces intermediate states of entirely new atomic structure as, for instance, martensite or the nonhomogeneous stage of gold-copper. 5. X-ray analysis of intermediate states of gold-copper alloys and also in the precipitation of copper from supersaturated silver indicates that conditions of relationship between diffusion and lattice change depend on the grain size. From this it follows that a transformation of large grains takes place, in the first case, much faster, in the second case, much slower than in small grains. These principles coincide with observations.

According to Hanemann (8) there are three kinds of diffusion through a metallic lattice: 1. Perfusion, or migrating atoms that slide along straight lines without disturbing other atoms in the lattice (through interstices?); 2. The concentric diffusion in which the atoms migrate through openings in the lattice or through exchange of place with other atoms to the nuclei points of the new type of crystal that is being formed (coalescence of Fe_3C at A_1?); and 3. The parallel diffusion in which the direction of movement is the same for a large number of atoms. In gamma mixed crystal the carbon moves with high velocity by perfusion. In alpha iron, (as carbide?) by diffusion (type 2) with low velocity. Since B. A.

Rogers (9) has observed the A_3 change to take place in waves crossing individual crystals it may be assumed that the second stage in the gamma-alpha transformation involves diffusion of the third type. (This will be referred to later in an explanation for the formation of two kinds of pearlite, lamellar and spheroidized.)

What is the Nature of Allotropy?

Many of the manifestations and effects of allotropic changes are accurately known. Various functioning mechanisms have been suggested. However, the ultimate cause (or causes) of allotropic changes, as we know them in various alloys, remains a matter of conjecture. Although the metallurgist, primarily interested in the manifestations, leaves the study of the causes to the physicist, it is of interest to note something of what is being accomplished in this complementary field.

In 1925, Webster (10), studying the magnetic properties of iron crystals, came to the conclusion that the molecular field (similar to that of the metallic lattice structure) is a stable property of the crystal and is affected considerably by the presence of impurities. Support was found for the view that the molecular field is not due to magnetic forces.

Also in 1925, Jones and Ingham (11) published the results of calculations of certain crystal potential constants. The law of force between atoms is expressed as a series of inverse powers of the distance between atoms—probably the most general form in which the force is ever likely to be expressed. The law of force is repulsive according to one inverse power of the distance and attractive according to another. To cause formation of a crystal lattice the repulsive field must fall off more rapidly than the attractive. Thus the face-centered cubic has less potential energy than the body-centered, and the body-centered less than the simple cubic. (According to this, then, alpha iron (the most stable) should be face-centered cubic and gamma should be body-centered cubic. Since the reverse is true we must qualify the statement of Jones and Ingham so that it holds if all the forms have the same interatomic force strengths. Thus, the forces between alpha iron atoms must be greater than the forces between gamma iron atoms to maintain a system that would otherwise be unstable).

Studying the distribution of electrons in a metal, Lennard-Jones

and Woods (12) published some interesting interpretations in 1928. Lines of equal potential and electron density were plotted for two dimensions of a lattice for a pure metal. Near a positive nucleus the equipotential lines are approximately circles. These are gradually deformed nearly into squares until a critical potential boundary is reached. This boundary, enclosing nuclei in cells, extends throughout the crystal. Electrons along this boundary may be regarded as shared, for they cannot be regarded as belonging to one nucleus more than another. The shared electrons form a lattice array which interpenetrates that of the nuclei. This provides some justification for the model of a metal proposed by Luideman and Thomson (13) in which the valency electrons form a rigid lattice interpenetrating that of the atomic cores. The system proposed by Lennard-Jones and Woods, however, is not a static one even at absolute zero.

In 1930 Stearns (14) published the results of a study of ferromagnetism. The results of other investigators indicate that neither minute crystal aggregations nor the chemical molecule nor the Rutherford type of atoms as a whole can account for ferromagnetism. New experiments show that it is highly improbable that electrons revolving in any of the orbits are responsible for ferromagnetism. Evidence is also against the conclusion that the nucleus may account for magnetic properties. It therefore appears that the ultimate magnetic particle should be identified with the spinning electron. Thus there may be distinct differences between the cause of magnetic changes and the cause of lattice changes.

In 1930 Slater (15) published an article concerning cohesion in monovalent metals. The theory of metallic structure of Summerfeld, Heisenberg, and Bloch, is carried far enough to explain cohesive forces and calculations are made for atoms with one valence electron, particularly for metallic sodium. The numerical results are in qualitative agreement with experiment. It is found that the forces in general are of the same nature as those met in ordinary homopolar bonding, discussed by Heitler and London, except that the purely electrostatic force from penetration of one atom by another is relatively more important and the valence effect from the exchange of electrons relatively less important than in diatomic molecules. In connection with conduction, it is shown that a definite meaning can be given to free electrons, that they are necessary to conduction, and that a method can be set up for computing their number, which is rather small compared to the number of atoms. It is shown that a

metal like an alkali cannot be ferromagnetic, for atoms at such a distance that the interatomic forces keep the metal in equilibrium are too close to be magnetic. For ferromagnetism, rather, it seems necessary to have one group of electrons responsible for cohesion, and another group, of smaller orbit and therefore relatively farther apart, producing the magnetism. This situation is actually found only in the iron group and the similar groups.

Since a crystal is sometimes regarded as a polyatomic molecule it is of interest to consider another article (16) published by Slater in 1931. Two atoms containing all their electrons in closed shells repel each other. If, however, each atom has one wave function containing only one electron, rather than two of opposite spins, attraction is possible. This actually occurs if the spins of the electrons in question in the two atoms are oppositely directed. The attraction pulls the atoms together until the wave functions from which electrons are missing overlap as much as possible, when equilibrium occurs. In consequence of resonance the charge concentrates at the place where the functions are overlapping, and in an approximate way we may consider that the two electrons of opposite spin, spending their time in this region, form a closed shell. This is a homopolar valence bond, and two electrons forming such a bond are inactive in forming further bonds, just as if they were in closed shells within a single atom. Structural models have been worked out for tellurium, bismuth, arsenic, antimony, carbon, silicon, germanium, tin and lead.

During study of electronic energy levels Hume-Rothery (17) in 1931 discovered a general law governing simple relations between the interatomic distances in crystals and the atomic numbers and electronic quantum numbers of the atoms concerned. If Z is the atomic number, the interatomic distances vary as $1/Z$, $1/Z^2$, $1/Z^3$, and $1/Z^5$ for the elements at the beginning of the first to fourth periods. The electronic levels vary linearly with Z^2, Z^4, Z^6, Z^{10} for electrons of the outermost group of electrons of the atomic core or ion.

Besides the work being done in studying attraction between atoms, research is also being made upon the types of repulsion that may exist. Tomlinson (18) regards the repulsion between atoms not as a central force at all, but rather as a quasi-elastic effect analogous to the type of force exerted mutually by two elastic spheres when deformed by being forced together. This repulsion is determined by the proximity of approach of the atom "boundaries."

From the evidence at hand it is apparent that we do not yet

understand the absolute nature of the laws that hold metallic atoms in lattice positions. Until we do know fully these laws we cannot understand the ultimate nature of the lattice changes that occur at allotropic points. Fig. 2 may be used to illustrate the situation until we know further facts. The three curves represent the vibrational lattice functions of alpha, delta, and gamma iron. These overlap so that as iron is heated along the alpha function to a temperature of

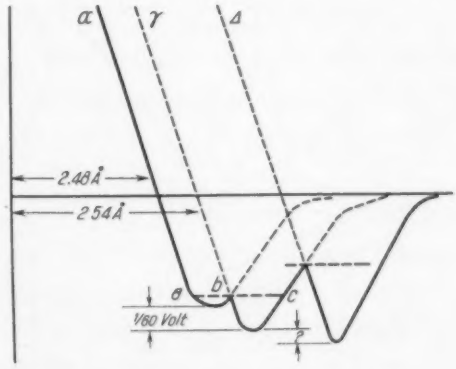

Fig. 2—Illustrating Lattice Changes that Occur at Allotropic Points.

900 degrees Cent. + (1650 degrees Fahr.) for pure iron it shifts over at point "b" to the more stable gamma function which it follows up to a similar overlapping function for delta iron. These functions possess similar thermal (expansion) variations and are differentiated by the difference in distance of closest atomic proximity. The difference in energy contents of the gamma and alpha systems is represented by the difference in the minima of the curves (about 1/60 of a volt according to the heat evolved at Ar_3. Fig. 2 is qualitative only and not drawn to any scale. It is suggested that 1/60 of a volt may be the balance of several inneratomic reactions instead of only one.

Some Applications of the Two-Stage Mechanism on the Allotropic Change in Iron

A useful mechanistic theory must successfully apply to a system as it may be affected by various factors. It is of interest, then, to apply the two-stage mechanism of allotropy to various ferrous problems and to suggest its application to others as future data become available.

On Martensite

In 1926 Hanemann and Schrader (19) presented a theory accounting for the variety of structures obtained in quenched steels of various carbon contents. Fig. 3 is a copy of their iron-carbon diagram showing the lines of the metastable martensite system. A description of the fields follows:

(a) Steels with less than 0.10 per cent carbon crystallize partly

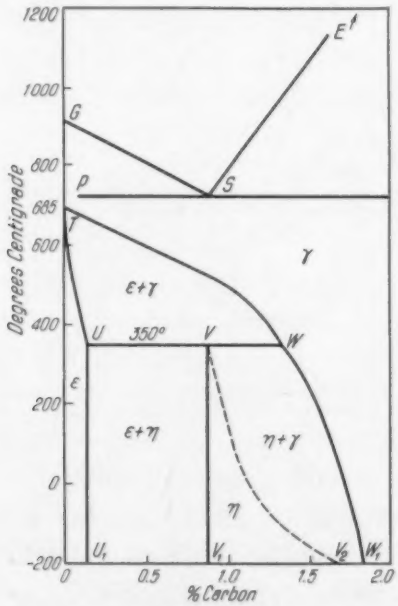

Fig. 3—Iron-Carbon Diagram (After Hanemann and Schrader).

needle-like and partly polygonal. This is explained by partially complete and partially incomplete equilibrium conditions in the field UTW.

(b) From 0.10 to 0.90 per cent carbon the quenched structures contain mixtures of two types of martensitic needles, the epsilon (or low-carbon) and the eta (or high carbon) forms.

(c) Excess austenite in quenched steels of 0.20 to 0.90 per cent carbon may result from incomplete reaction at UVW.

(d) In steels of over 0.90 per cent carbon austenite forms on quenching, in amount increasing with carbon content.

(e) It is observed that the alpha ferrite needles and net work, even in low carbon steels, will etch differently than the martensite needles. This is explained by the appearance of iron in the alpha, epsilon, and eta modifications.

Further publications of work directed by Hanemann (20, 21, 22) yield the following points:

(f) The eta phase of martensite corresponds to the tetragonal phase described by Sachs and others.

(g) Cementite is formed only at the second transformation of martensite.

(h) The state between the first and second transformations of martensite contains a distorted alpha iron lattice with interspersed and adsorbed carbon atoms.

(i) In a 1.6 per cent carbon steel it was deduced from structural changes with heat treatment that the eta phase carried a carbon content of about 1.1 per cent. (The austenite must then have been supersaturated.)

(j) Austenite of high carbon steel from below 200 degrees Cent. up to the temperature of incipient martensitization is extraordinarily stable. At higher temperatures it breaks up, without a transition stage, into ferrite and cementite (troostite?). The beginning of martensitic crystallization is definitely related to a temperature that depends on carbon content. It takes place in a range in which equilibrium between austenite and the eta phase occurs for each definite temperature. This gamma to eta transition is little affected by the speed of cooling. This proves that the martensite formation is a process entirely independent of the transition of austenite into ferrite and cementite and follows its own laws.

Applying the two-stage mechanism of allotropy to this metastable martensitic system it seems that:

(a) Epsilon, having the same lattice as alpha iron, carries carbon atoms probably interspersed in the lattice interstices. Both stages of allotropic change have been completed.

(b) Eta, identified as the tetragonal type described by Sachs, has passed completely through the lattice-directional change, but only partially through the diffusion shift from gamma to alpha iron. Although carbon solubility is denied in this form, the carbon atoms are trapped in locations dependent on those held in the original austenite. It is from this form that most of the cementite is precipitated.

(c) It is, therefore, easier to regard epsilon and eta as structural variations of martensite rather than metastable forms of iron atoms differing from alpha iron atoms.

(d) Of course, it is highly probable that some Fe_3C forms in

all quenched carbon steels although it may not be found microscopically.

(e) The other conclusions of Hanemann and his associates follow as readily upon this simplified foundation.

It is also interesting to note the results of work by Einar Öhman (23). X-ray investigations with high dispersion focusing cameras have shown that the tetragonal martensite lattice dimensions vary continuously with the carbon content. This result indicates that the tetragonal martensite is a supersaturated solution of carbon in alpha iron, and that the carbon content is the same as that of the austenite from which it forms. The hypothesis is advanced that the structure consists of C_2 groups oriented parallel to the tetragonal axis. This explains the observed density, volume increase with carbon content, and the elongation of one of the crystal axes. Decomposition on tempering takes place continuously with a progressive decrease in the axial ratio.

By means of thermodynamics F. H. Jeffery (24) arrives at the conclusion that austenite is a solid solution of monotomic carbon in gamma iron and not of Fe_3C in iron.

The Austenite-Pearlite Transformation

Just as the austenite-to-martensite change is a function of gamma iron, atomic carbon, and alpha iron, so is the austenite-to-pearlite change a function of gamma iron, atomic carbon, alpha iron and Fe_3C.

The two stages of allotropy may occur successively so closely together as to appear to be simultaneous, or the diffusion stage, on cooling, may lag somewhat behind the lattice directional change. Cooling rates and impurities may variously affect the amount of lag.

In a eutectoid steel, if the two stages are separated by an appreciable lag so that the lattice directional change well precedes the diffusion shift and carbide precipitation, the carbide formation will occur in a lattice that is essentially alpha in character. The carbide would then probably form by concentrical diffusion in which the atoms (or molecules of Fe_3C) migrate with low velocity through openings in the lattice or through exchange of place with other atoms to the nuclei points of the new type of crystal that is being formed. Thus, spheroidized cementite would result. (Granular pearlite.)

If, however, the lattice, diffusion, and carbide formation reactions occur simultaneously, straight line diffusion of high velocity may be possible through unchanged austenite and the transition stage of alpha iron, so that cementite plates would form. (Lamellar pearlite.)

Fig. 4 shows the thermal analysis of an abnormal steel and is to be compared to Fig. 5 showing the thermal analysis of a chemically

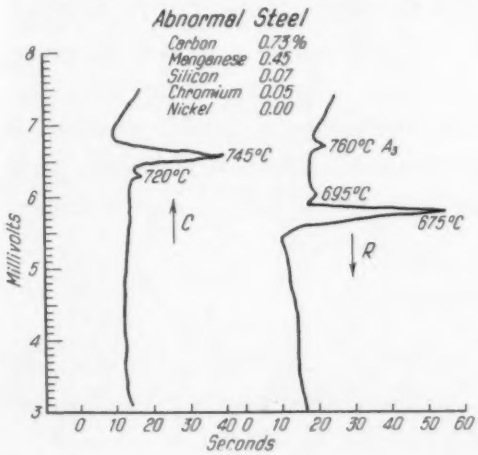

Fig. 4

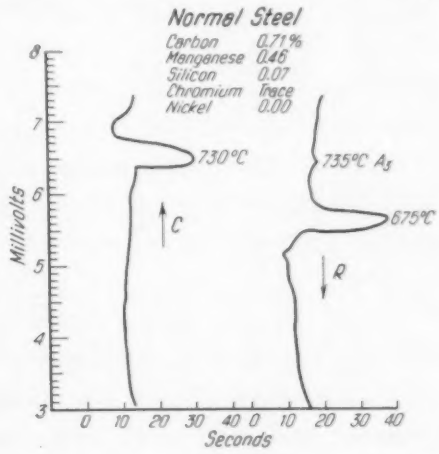

Fig. 5

Figs. 4 and 5—Thermal Analysis Results of an Abnormal and Normal Steel.

similar (by ordinary analysis) normal steel. It is to be noted that the two stages of allotropy are separated by definite lag in the abnormal steel while occurring simultaneously with the carbide reaction in the normal steel. It is suggested that this difference perhaps caused by whatever specific impurities may be present, may account for the structural differences found in the two types of steel.

Drawing of a Quenched Steel

Hanemann has shown that martensite may form in the initial quench of a steel and upon transformation of retained austenite in draws up to about 200-250 degrees Cent. If a steel, containing retained austenite as well as martensite, be drawn at higher temperatures (above 250 degrees Cent.), the carbide will form from the martensite by slow concentric diffusion through alpha iron and spheroidal cementite particles will result. It is probable that the retained austenite will transform similarly and, without passing through the martensitic stage, will yield spheroidal particles of cementite plus alpha iron. (troostite and sorbite.)

Transitions in Alloy Steels

One example will be considered; that of the tungsten high speed steels. These steels, when properly drawn, usually show what appears to be an austenitic matrix bearing carbide or tungstide hardening particles. Yet these steels are surprisingly magnetic. It is suggested that the lattice directional change, or first stage of allotropy, has occurred, but that the high alloy content and dispersed hardener have prevented the occurrence of the diffusion, or second stage of allotropy. The alpha iron atoms are thus free to undergo the magnetic inneratomic (?) change and become magnetic alpha iron atoms restricted largely to a gamma iron lattice structure. This may similarly be true of some of the structures to be found in the highly alloyed magnet steels.

Conclusions

1. Further justification of two-stage allotropy is offered in thermal analysis data from a special series of thirty-two steels. [Some evidence had been given in a previous publication(1).]

2. Recently published data of other investigators is considered from the viewpoint of a two-stage allotropic mechanism.

3. The cause, or governing law, of the change in lattice directional forces is not yet known.

4. The two-stage mechanism, when applied to the metastable martensitic system of Hanemann and Schrader, makes the postulation of metastable forms of iron unnecessary and may account for the distinct variations of martensitic structure.

5. The two-stage mechanism may be applied to other phenomena and problems, such as: the austenite to pearlite transformation, formation of granular and lamellar pearlite, normality and abnormality in steels, structures in quenched and drawn steels, and structures and transitions in some of the alloy steels.

Acknowledgments

The authors wish to thank Dr. S. L. Hoyt and Dr. Saul Dushman for many pleasant and enlightening discussions.

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DISCUSSION

R. S. ARCHER[1]: I know you will all realize that we have been listening to a paper dealing with the very fundamentals of steel metallography, and therefore one which deserves our careful thought. The authors have again presented their view that the allotropic changes take place in the manner as shown by the three typical sets of heating and cooling curves.

Perhaps the first question in matters of this kind is a question of facts. We may inquire whether there was any circumstance connected with the thermal analysis which may have shown a two-stage reaction, whereas really only one point existed. We may also inquire as to the exact nature of the steels used in this work.

[1]Chief of metallurgical research, A. O. Smith, Corporation, Milwaukee, Wis.

I hope Mr. Howard Scott, who is present and who has had a great deal of experience in thermal analysis, may bring out some views regarding the significance of the curves actually obtained.

I would also like to ask Dr. Harrington a little later if he would describe again for us the exact manner of preparation of these steels, in particular stating whether the hydrogen used was absolutely dry or contained some water vapor. I want to bring out that description particularly inasmuch as these are unusual steels.

Specimens were not produced by the usual processes but by a special process of diffusion. The question whether the hydrogen was particularly dry or not was raised to bring out whether there was a possibility that the specimens might have become saturated with oxygen during that 6-day heating.

The authors have shown one curve of a normal 0.70 per cent carbon steel in which no double cusp was obtained. Enough runs of this kind would indicate that the method is not erroneously giving double cusps where they do not belong. It seems very interesting that the double cusp was obtained with an abnormal steel and not with a normal steel. That is very suggestive and it is unfortunate that Dr. M. A. Grossmann and E. C. Bain and others who have made a special study of that are not present to comment on this phase.

Now let us assume that the double cusp is a reality. It seems that the authors' suggestion regarding interpretation are very significant and may point the way to the explanation of structures and also perhaps an explanation of abnormality.

I wonder if someone has ideas on the interpretation phase of the paper.

HOWARD SCOTT[2]: I do not feel in a position to discuss this paper in a critical way at all, since it is was not preprinted, but I would like to make a few comments, having done a good bit of work along this line at the Bureau of Standards. There we worked with iron-carbon alloys melted under conditions not so good as we have available now. Nevertheless, a considerable amount of work was done by thermal analysis. While we were not prepared, as a result, to present an iron-carbon diagram, we did learn a lot.

For one thing, I do not recall any case where we got double transformation associated with the A_1 point. We would get erratic points occasionally. That seems to be a characteristic of the thermal analysis method.

On the other hand, at the A_3 point we would get quite consistently a double point in low carbon alloys. This point was quite definitely due to decarburization. We would not get it on the first heating, as a rule, but after reheating it would show up more prominently. There is a Bureau of Standards paper by Dr. H. S. Rawdon and myself showing decarburization effects obtained in thermal analysis that way.

A little more information on the composition and preparation of the steels as the chairman has remarked would add to the discussion. Attention might be called to the authors' diagram based on Hanemann and Schrader's work because in the next paper on the program we present a similar type of diagram and it is very different in appearance.

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[2]Section engineer, special problems section, research laboratories, Westinghouse Electric and Mfg. Co., East Pittsburgh.

BRADLEY STOUGHTON[3]: If the discussion of this phase of the authors' paper has been completed, it seems to me that, in the absence of Professor Sauveur, I should bring up for discussion another point which is a fundamental basis of the subject.

The allotropy of elements is a phenomenon which has been recognized for a long time. It has been known much longer than has the process of X-ray spectrometry, and, therefore, the form of space lattices of metals. But now the X-ray spectrometrists seem to assume that a new definition for allotropy may be established on the basis of space lattice form alone.

I am aware that most authors speak of the alpha and gamma modifications of iron changing one into the other and that many metallurgists now assume that the beta modification is not a separate allotropic form because it has the same space lattice as the alpha modification and not withstanding that it differs from it radically in other physical properties, such as, for example, its magnetic permeability. It seems pertinent to ask: If the beta nonmagnetic form of body-centered space lattice is not an allotropic modification quite distinct from the body-centered alpha form, then what is it and why are some of its physical properties notably different from those of the alpha modification? There are many able metallurgists here who can discuss this question if they will.

Authors' Closure

The discussion contributed by Mr. Archer and Mr. Scott is sincerely appreciated by the authors. Characteristically, several important questions have been asked and pertinent points emphasized. In answer and for elaboration the following statements are offered. In replying to Mr. Archer may we say that the use of the modified Rosenhain furnace is described in a previous paper by the authors (loc. cit.). If stray fields (or other effects) were existent to cause the double cusps it would seem exclusive of these that doubling would occur only for the A_3 and A_1 transformations in the unique and consistent manner observed without similarly affecting at times the A_2 and A_{cm} thermal points. This consistency extended throughout the series of 32 special steels for both original and check runs. A similar apparatus, of different dimensions, built and used in the General Electric Research Laboratories, has yielded similar curves for the allotropic points in cobalt and some cobalt alloys, and in various plain carbon steels.

The exact manner of preparation of these steels is best described in detail in the previous paper by the authors. The methods and apparatus were those used by Professor E. D. Campbell at the University of Michigan to produce iron-carbon alloys of definite predictable carbon content. The cycle requires a 6-day heat in hydrogen at 960 degrees Cent. (1760 degrees Fahr.). Both oxygen and water vapor were removed from the hydrogen before this gas entered the furnace in which the carbon-iron equilibrium was being developed. The samples had origin from a special heat of Armco iron.

In reply to Mr. Scott—Double cusps were observed for all A_3 points until mergence of A_3 with A_2 took place, following which only single cusps were

[3]Professor, department of metallurgy, Lehigh University, Bethlehem, Pa.

observed. As described in the present paper, double cusps were also observed at A_1. The data were obtained from original and confirming check runs on samples heated and cooled in a vacuum indicated by a pressure of 10 millimeters of mercury. Microscopic inspection of samples before and after thermal runs failed to show the slightest decarburization. Surfaces of the samples did not show any indication of oxidation during the runs.

The diagram by Hanemann and Schrader, describing various states of martensite, was used by the authors only as one example for the application of the two-stage allotropic mechanism. It may well be that the diagram, as it may be revised by Mr. Scott in the next paper, remains subject to application of this theory.

The discussion contributed by Professor Bradley Stoughton raises not so much a point for argument as a request for definition and an encouraging demand for continued research. The authors wish to thank him for his interest and to offer, in conclusion, some definitions in the hope of clarifying future argument.

Magnetic transformation, or, if one prefers, magnetic allotropy, appears to involve solely an inneratomic change. Electron spin might be an example of such an inneratomic change. Atomic fields are apparently changed without directional effects on the lattice itself.

Lattice transformation, more commonly specified as allotropy, appears to involve an interatomic change as the result of a directional type of inneratomic change. An example of this type might be pictured as a shift in the angular relationship of the orbital planes of the outer electrons without, however, effecting any change in the energy levels of the electrons involved. The change in interatomic forces might thus require a shift in lattice to attain the new equilibrium state.

The examples have been cited only for the purpose of illustrating the possible difference between a magnetic transformation and a lattice transformation. The true causes of these transformations are probably quite different from the examples cited and are certainly unknown to the physicists at the present time.

The authors wish to suggest that the adjective "allotropic" be applied to all atomic changes involving chiefly a change in the type of lattice structure; that the adjective "magnetic" be applied to all transformations involving chiefly changes in magnetic properties.

INTERNAL FRICTION IN IRON AND IRON ALLOYS

By R. H. Canfield

Abstract

The author describes a method of measuring the dissipation of energy in a tubular specimen of metal when carried through cycles of alternating torsional stress. A method of plotting results is used, where the half width of the hysteresis loop is plotted against the stress amplitude. This curve is "friction stress" plotted against "elastic stress" and its slope is a coefficient of internal friction.

In alpha iron the curve shows four critical points, at each of which new mechanical phenomena manifest themselves.

The author advances a partial explanation of these facts, based on intracrystalline slippages of the order of atom diameters.

Data are given covering the internal friction behavior of the purest iron, of iron and mild steel after plastic deformation and of a few alloy steels. A few numerical values of internal friction coefficients are included.

Introduction

INTERNAL friction is a property common to all solids but includes a number of phenomena between which it is necessary to draw clear distinctions at the outset. Whenever a material is carried through a cycle of strain it exerts smaller stresses during the removal of the strain than it did during the application of the strain. If we plot the stresses against the strains as in Fig. 1, we find that instead of retracing the single straight line AOB as it would do if Hooke's Law were exactly obeyed, it traces a loop such as PQRS, which represents the symmetrical condition which exists after a number of strain-cycles have been performed. Of course the area of the loop represents work absorbed by the specimen and not returned in the form of elastic energy. The whole picture bears an

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exact similarity to the hysteresis loop in magnetic materials, and in fact the term "elastic hysteresis" is often used to describe the phenomenon.

A fact that must be borne in mind from the outset is that the dissipative or nonelastic forces at play here are only associated with

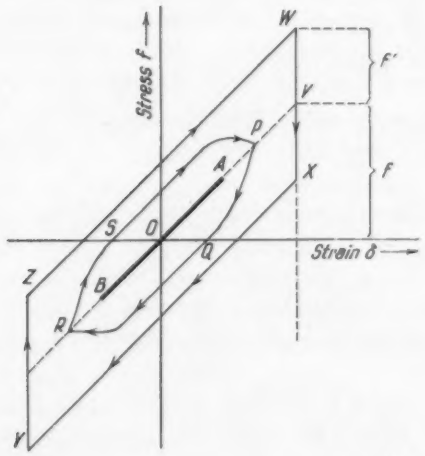

Fig. 1—Hysteresis Loops in Stress-Strain Cycles.

shearing strains. Even the most complex strain distribution can be divided uniquely into two parts; dilatation or change of volume, and distortion or change of shape.[1] For instance, when a rod is simply stretched, the elastic energy associated with distortion is to the energy associated with dilatation in the ratio E/(3N-E) where E is Young's modulus and N is the shearing modulus. For ordinary metals this ratio is about 5 to 1, so that even for simple tension the shear-strain plays a predominant role, and internal friction will be in evidence. On the other hand when a metal is subjected to hydrostatic pressure the strain is entirely dilatation and no internal friction has ever been proved to exist for such strains. In this respect internal friction in solids is quite analogous to viscosity in liquids, where, as is well-known, the frictional stress is proportional to the rate of change of shear strain.

For this reason, as well as because it leads to a simple mathematical treatment, some writers have assumed without sufficient experimental evidence that internal friction in solids was exactly

[1]A. E. H. Love, "Mathematical Theory of Elasticity," Cambridge, 1906, p. 47.

analogous to viscosity in liquids and have made the frictional stress proportional to the rate of change of shear strain. That this is not the case is proved by the researches of Kimball and Lovell,[2] of Quimby[3] and of Föppl,[4] who have shown that the loss of energy per cycle is independent of the frequency of the cycles, and hence of the strain velocity, at least for ordinary metals within their elastic ranges. This was also known to Lord Kelvin.[1]

At this point it is only proper to say that there is abundant evidence of truly viscous stresses at work (a) in supercooled liquids and ultra-microgranular solids, like sealing wax and glass, (b) in certain crystalline materials like marble, (c) in metals strained beyond their elastic limits and (d) in metals subjected to even small loads at high temperatures (creep). This type of dissipative stress belongs in the realms of plasticity. It is unimportant in ordinary metals at ordinary stresses, temperatures, and frequencies, and we shall not discuss it here.[5]

Returning to the diagram of Fig. 1, the exact shape of the hysteresis loop is difficult to measure, since the width of the loop may correspond to a strain of a millionth of an inch per inch or less. What evidence exists[6] points to a loop with nearly straight and parallel sides. Since most experiments, including those reported here, measure only the work absorbed or the area of the loop, it seems convenient to assume that the loop is a parallelogram like WXYZ. The half-width of the loop, f′, we call the friction stress, while its total height f we term the elastic stress or stress-amplitude. Suppose that as a result of an experiment we have found that in a stress-cycle such that w units of energy per unit of volume is stored up at either end of the swing, an amount of energy w′ per unit of volume is dissipated. It is easy to verify that

[1]Love, loc. cit. p. 115.

[2]A. L. Kimball and D. E. Lovell, *Physical Review*, Vol. 30, 1927, p. 6.

[3]S. L. Quimby, *Physical Review*, Vol. 25, 1925, p. 4.

[4]O. Föppl, *Ztschf. d. Ver. Deutsch. Ing.*, Vol. 70, 1291, 1926 and other papers cited in Ref. 5.

[5]For a very good treatment and complete bibliography of the whole subject see Hans Fromm, Handbuch der Physikalischen und Technischen Mechanik, Leipsig 1931, Band IV. 1. Hälfte, p. 436.

[6]J. H. Howard and S. L. Smith, Proceedings of the Royal Society, London (A), Vol. 107, 1925, p. 113.

$$w = f^2/2E \quad (1)$$

and

$$w' = 4ff'/E \quad (2)$$

where E is the proper elastic modulus. From these formulas it is easy enough to compute the corresponding values of f and f′.

In some cases it is found that w′ is proportional to w, leading to Kimball's[2] formula

$$w' = \xi f^2 \quad (3)$$

where ξ is Kimball's constant of internal friction. This in turn leads to an alternative expression

$$f' = \phi f \quad (4)$$

a formula proposed by the author,[7] wherein Φ is the "coefficient of internal friction." Another modulus or constant of internal friction due to Föppl[4] is equivalent to the energy-loss per cycle per unit volume (kg-cm units). It is open to the same objections noted below for Kimball's ξ, except that it is not alleged to be a constant. The

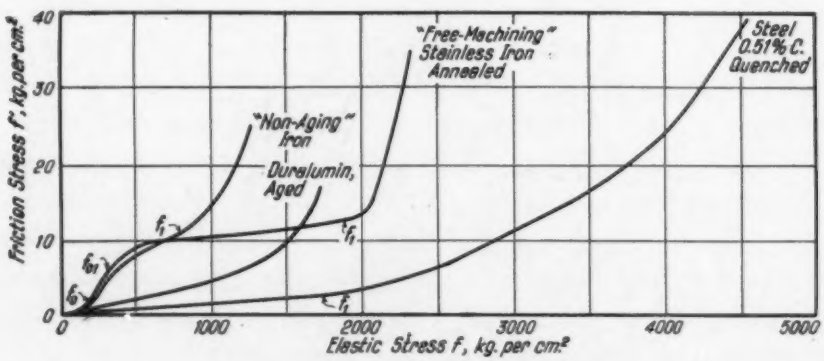

Fig. 2—Typical f′-f Curves.

principal advantage of Equation (4) over Equation (3) is that Φ is dimensionless and hence independent of systems of units, which ξ is not. Unfortunately both equations labor under the disadvantage of being untrue, or at least of being true in only a few cases. Were they valid, the hysteresis loops would increase equally in height as in width, and the curve f′ versus f would* be a straight line, like curve (a) in Fig. 2. As a matter of fact curves of other shapes, like (b), (c) and (d) are at least as common.

[7] R. H. Canfield, *Physical Review*, Vol. 32, 1928, p. 3.

*In the present paper the author plots f′ as ordinate, f as abscissa, contrary to his practice in his two previous papers. The change is for the sake of avoiding a natural confusion of an f′ versus f diagram with a stress-strain diagram.

It is still possible to estimate a finite value of Φ for $f = O$, which we may call the "initial coefficient of internal friction," by analogy with the "initial permeability" used in magnetic studies. A more complete theoretical discussion will be found in the author's two previous papers.[7] [8]

Experimental Technique

The earliest experimenters on internal friction measured the rate of decay of elastic vibrations: either of torsion pendulums controlled by a wire made of the material under study, or of tuning forks made of the material. Both of these methods are open to the

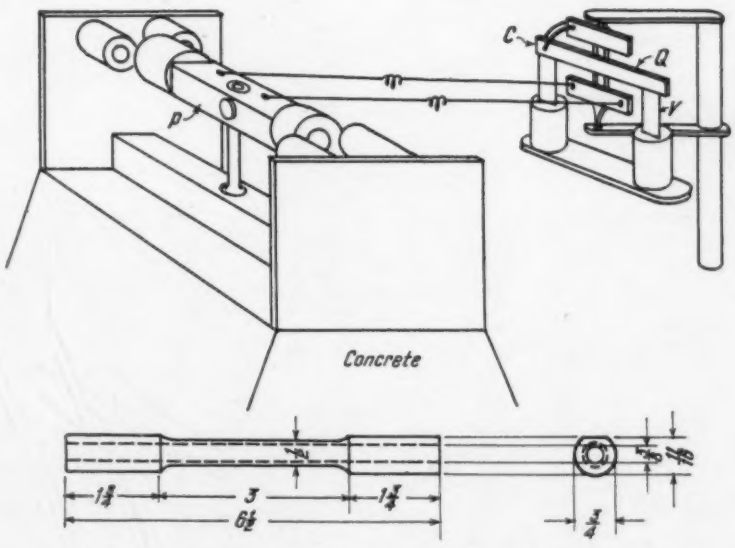

Fig. 3a—Sketch of Apparatus and Tubular Specimen.

same objections: 1—different parts of the specimen are stressed to different degrees; 2—during the process of getting the decrement the stress-range is changing. Both of these deficiencies lead to the same sort of inaccuracy—a smoothing out of the f′ versus f curve so that it appears straighter and more uniform than it actually is.

The method used in the ensuing experiments is to make the specimen the elastic control of a large torsion pendulum which is maintained in a steady state of vibration by electromagnetic forces. These forces can be accurately estimated from the readings of ammeters. The apparatus is illustrated in both Figs. 3a and 3b.

[8]R. H. Canfield, Proceedings III International Congress of Applied Mechanics, Stockholm 1931, Vol. II, p. 331.

The specimen itself is a fairly thin-walled tube so that if due allowance is made for the ends we may say that all parts of the specimen are going through the same stress-cycle. The stress f is determined from the frequency of vibration of the pendulum, its moment of inertia, the amplitude of the vibration, and the "section modulus," or physical dimensions of the specimens. The friction stress f′ is

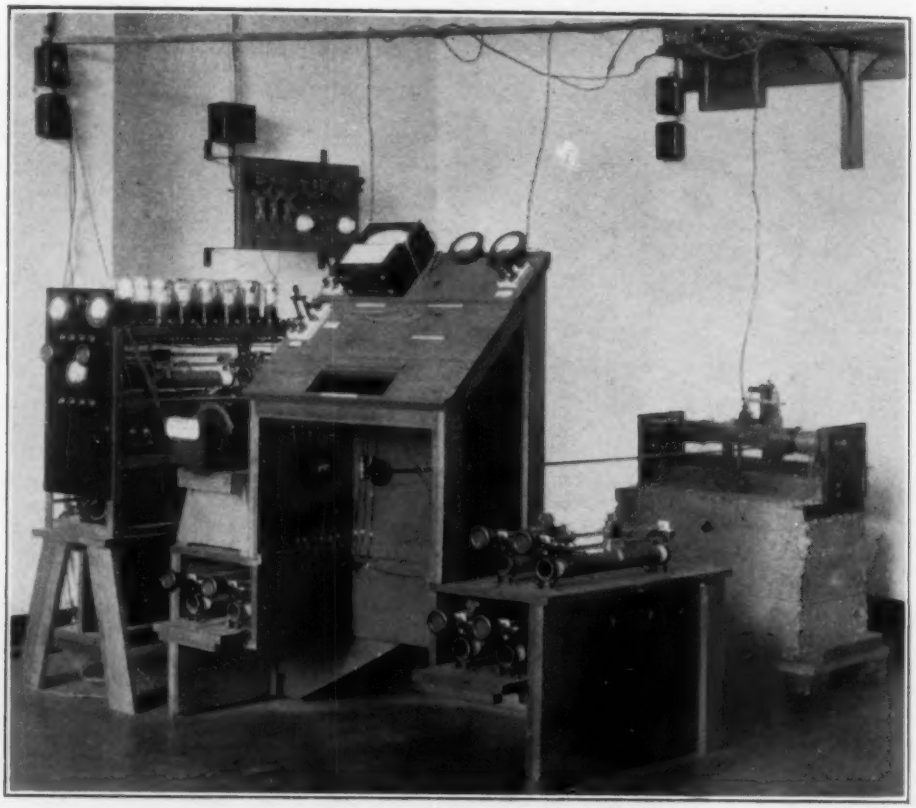

Fig. 3b—Photograph of Testing Apparatus.

determined from the currents flowing in the fixed and movable electromagnets, and the section modulus of the specimen. A complete description and theoretical discussion of the apparatus will be found in the author's previous papers,[7] [8] except for a change in the method of driving. The new method is illustrated in Fig. 3a and Fig. 4. Here P is the pendulum, with its windings. The main pendulum is coupled by light springs to a subsidiary very light pendulum Q carrying contacts C by means of which proper values of potential are applied to the grids of a bank of 28 vacuum tubes (type 71-A) connected in parallel. The plate current of these tubes passes through

the primary of a transformer T, and the alternating component is passed on to the windings of the main pendulum from the secon-

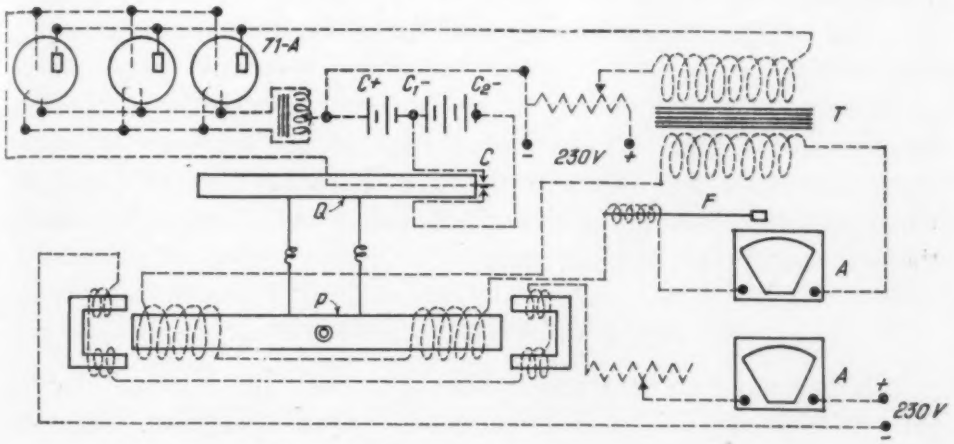

Fig. 4—Diagram of Electrical Circuit.

dary. By varying the plate voltage and number of tubes in parallel, a wide range of power is obtainable.

It is very important that the alternating current driving the main pendulum shall be in the correct phase relation to the motion of the pendulum, in order to secure maximum amplitude. This is accomplished in a very satisfactory manner by having vanes V attached to the movable part of pendulum Q and dipping into oil cups which are raised and lowered by a rack and pinion device controlled from the observing desk. By adjusting the height of these oil cups, the correct phase relation is easily realized.

Currents supplying both the fixed magnets and the pendulum windings are measured by ammeters A. The frequency is measured by the specially designed tungsten-reed frequency meter F. The amplitude of the pendulum's vibration is measured by the width of the band of light formed by the image of a fixed lamp filament, formed by a concave mirror M attached to the pendulum, and focussed upon a ground glass scale in the observing desk. In this manner the pendulum is made to drive itself at its own resonant frequency.

Experimental Results

General. The curve f′ versus f is far from being dependent only on the chemical nature of a metal or alloy. Instead, it is primarily a function of the physical condition of the specimen. Among

the factors which influence the form of the curve are: 1—the space-lattice or crystal class of the metal, or of the various solid phases in the metal; 2—the grain-size of the metal; 3—the amount of intra-granular strain or hardening, whether strain-hardening, precipitation-hardening, or solid-solution hardening; 4—effects of plastic deformation or fatigue, which disappear after a certain lapse of time and 5—effects due to condition of surface and existence of internal cracks or stress concentrations, which may be considered extraneous to the true properties of the metal itself, but which, nevertheless, must be guarded against.

Pure Unhardened Alpha Iron

It is proper to commence this paper with the internal friction properties of alpha iron in its pure and unhardened state. The clos-

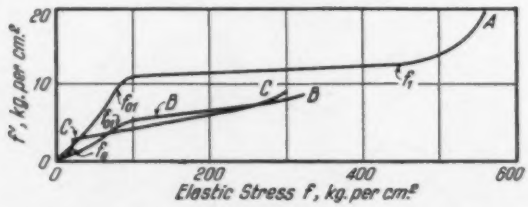

Fig 5—f'-f Curves Typical of Body-Centered Lattice.
A—Armco Iron Purified 92 hours in Hydrogen at 1200 Degrees Cent.
B—Same Specimen 6 Hours Later.
C—Cast Brass.

est approach to this material that we have been able to obtain have been a few specimens made of Armco iron, subjected to a prolonged (48 to 120 hours) treatment in moist hydrogen at temperatures from 1100 to 1250 degrees Cent. (2010 to 2280 degrees Fahr.). The f′ versus f curve of one of these is given in curve (A), Fig. 5. This specimen had been hydrogen-purified for 92 hours at 1205 degrees Cent. (2200 degrees Fahr.) and cooled for 16 hours in the furnace. It had a grain size of about 3 millimeters and represents the extreme type of the pure alpha iron curve. Curve (B) in the same figure is the same specimen tested about 6 hours later. The change observed is due to hardening which resulted from making the previous experiment.

Knee Feature Characteristic of the Body-Centered Lattice

The knee marked f_{01} in the two curves seems to be a charac-

teristic feature of the internal friction curve for metal with body-centered space lattices. The evidence for this is as follows: the knee is always present in pure alpha iron and to a lessening degree in carbon steels which contain the alpha iron phase. It is likewise present in stainless iron containing 13 per cent chromium, which is also an alpha solid solution. It is present in beta brass (curve C, Fig. 5), which is a body-centered solid solution. It is absent in austenitic steels such as the 18 and 8 type, also in 38 per cent nickel steel (invar). It is also absent in alpha brass, which has a face-centered cubic lattice. It is absent in copper, zinc, aluminum, duralumin, phosphor-bronze, and in fact all the non-body-centered metals on which experiments have been made.

The Knee Influenced by Hardening Agencies

As already mentioned, the knee is straightened out and lowered by any hardening treatment. Even normalizing, which involves cooling rapidly through the gamma-alpha transition range, results in a marked flattening of the knee, due probably to the internal strains of recrystallization. Also minute traces of hardening impurities seem to influence it, for the unpurified Armco iron, even with the most drastic softening anneal, exhibits a much less marked knee than does the purified iron. The reader will therefore observe, in some of the curves which follow, variations in the height of the knee, which are due to variations in heat treatment. In particular he will note its complete erasure in quenched carbon steels and in drastically cold-worked steels. There is no evidence that grain-size, considered by itself, has any influence on the position of the knee in the curve.

A Hypothesis of the Mechanism of Internal Friction

There will be occasion hereafter to refer to certain discontinuities or changes in slope of internal friction curves such as the knee already described. Some of these are associated with important properties of the material. All of them are without doubt intimately related to the nature of the crystal lattice and to events which occur in crystal grains during the process of strain. Kidani[9] has in fact advanced a theory of internal friction which relates the phenomenon to minute slips along certain preferred planes and orientations. Such

[9] Y. Kidani, *Journal*, Faculty of Engineering, Tokyo Imperial University, February, 1931.

slips must be radically different from those which accompany the plastic deformation of metals, since they are invisible under the microscope, and occur while the metal is still essentially elastic.

It is possible that slips do occur, even in the elastic range, along certain preferred planes of the lattice; but instead of being large displacements, as in plastic flow, they would be very small (perhaps limited to exactly one atom diameter). Of course, they would occur, just as in plastic flow, on planes fairly widely separated, the material between the planes continuing to be quite elastic. The law governing the spacing of these planes remains quite unknown, just as it does in the case of plastic slip.

A rough calculation will illustrate the nature of this assumption. Suppose the material has a rigidity modulus E and the shear stress at which slip commences is f_o. Further let the slip planes be spaced a distance x apart, and the amount of slip (one atom diameter) be a. Then the work lost in executing a complete stress cycle, assuming the sliding to be reversible, will be $4f_oa/x$ per unit of volume. This is equal to $4f_of'/E$ (Eq. 2), so that

$$x = \frac{Ea}{f'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Thus if f′ is about 10 kg/cm², and E about 800,000 kg/cm², then x is of the order of 80,000 atom diameters, or roughly, 0.0025 centimeters (25 microns). Reasoning by analogy with the spacing of slip planes in plastic deformation, this spacing seems a very credible one.

Working on such an assumption, we would explain the occurrence of a critical point on the f′-f curve by saying that it corresponded to a stress at which the above described reversible slipping could commence along certain crystallographic planes and directions in the most favorably oriented grains, and that the further increase of f′ with f in a polycrystalline specimen was due to the successive involvement of more and more grains as the shear stress increased so as to attain the critical value in the less favorably oriented crystals.

In order not to commit ourselves finally to any scheme of identification of these critical points, we will merely identify them by the symbols f_o, f_1, etc., as occasion may require.

The f_o-Stress. The critical points, to which reference has just been made, are not, even in the fairly thin-walled specimens used

here, perfectly sharp. In fact, the stress f is calculated at the outer surface of the specimen. Since most of the specimens are of 1/2 inch outside and 3/8 inch inside diameter, a critical stress which is just commencing to evidence itself at a certain value of f does not reach the inner wall until f has increased to 4/3 f. Thus every critical point is stretched out over a range of 1/3 f. This is not the only manner in which these breaks may be smoothed out, however. If the metal is in a condition of initial internal stress, some grains will reach a stress f long before their neighbors, and the effects of a certain type of slip will spread over a long range of the curve. This is the reason that the critical points are much more plainly marked in fully annealed specimens than they are in specimens which have been cold-worked, quenched, or otherwise left in a condition of internal stress.

The f_0-Stress. As mentioned in a preceding paragraph body-centered metals are characterized by a knee in the f′-f curve. Both the upper and lower bends of this knee are discontinuities of the type just discussed. Neither of the critical stresses appears to have any constant value, varying greatly both with constitution and history of the specimen. Because the lower break is found in many metals besides iron, it is given a special designation f_0. The upper break, found only in body-centered metals, will be called f_{01}. Values of these stresses for commercially pure (Armco) and hydrogen-purified iron are as follows:

	f_0 kg/cm²	f_{01} kg/cm²
Armco	100	260
Hydrogen Purified	0	100

The f_1-Point. Beyond the knee just described there occurs a range of stress where the friction f′ remains almost unaltered or increases very slightly. This terminates very abruptly in alpha iron, but often more gradually in other materials, at a point marked f_1 in the diagrams. This point coincides roughly with the elastic limit, and appears to be the point at which true plastic deformation sets in. Lacking exact information on this question the author prefers to call it simply the "f_1 point." What is certainly true is that above this point the stress f′ increases with a high power of f.

Grain-Size Determines Position of f_1-Point. The stress at which the f_1 point occurs is an important property of the material, as it will be seen later that cyclic stresses of a greater amplitude

than f_1 leave a permanent effect on the properties, while lower stresses can be repeated indefinitely without producing measurable effects. In pure or nearly pure iron, such as Armco, the f_1 stress appears

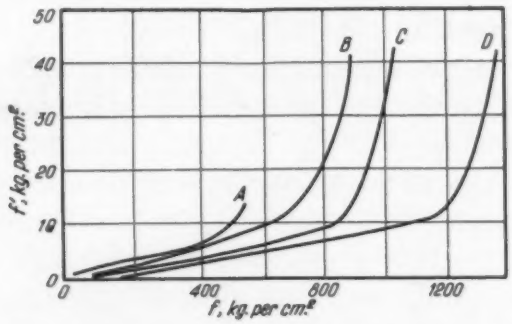

Fig. 6—Armco Iron Strain-Annealed to Produce Various Grain Diameters.
A—Grain Diameter 1.0 Millimeter
B—Grain Diameter 0.25 Millimeter
C—Grain Diameter 0.065 Millimeter
D—Grain Diameter 0.025 Millimeter

to depend mainly on the grain size. This is illustrated by Fig. 6, which shows curves for some purified and some unpurified Armco iron of various grain diameters.

Effects of Plastic Deformation. In the early stages of ex-

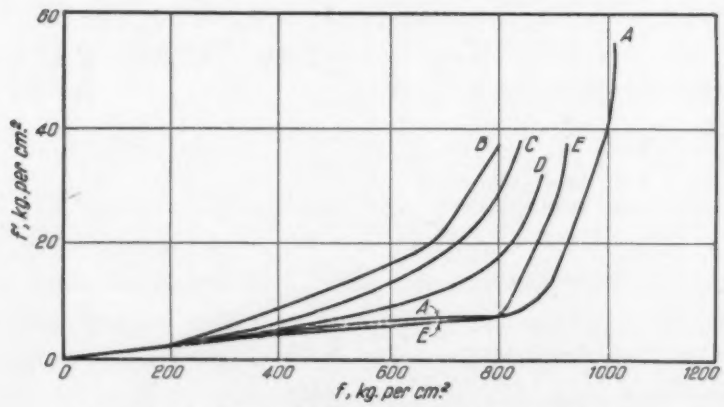

Fig. 7—Plastic Deformation and Recovery.
A—Original Condition.
B—Immediately After Overstrain.
C—1 Hour Later.
D—3½ Hours Later.
E—22 Hours Later.

perimentation with this apparatus, an accident occurred which led to some interesting observations. Through a mistake in making electrical connections a huge current passed momentarily through the pendulum windings. The result was to give the specimen of

unpurified Armco iron then in the machine a permanent twist of 4 degrees. The specimen then in use had screw-threaded ends; the operator accordingly replaced the pendulum in its central position

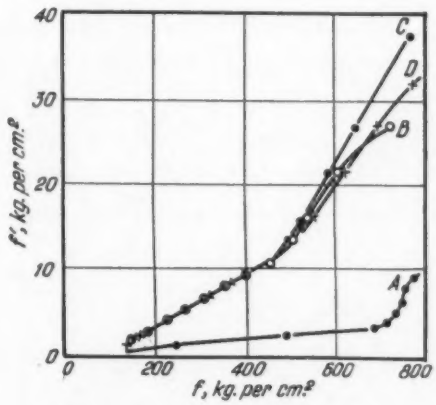

Fig. 8—Varying Amounts of Overstrain.
A—Original Condition.
B—4 Degrees Cold Twist.
C—7 Degrees Cold Twist.
D—10 Degrees Cold Twist.

and at once proceeded to take data for a curve. The result was curve (B) of Fig. 7. Curve (A) was the curve for the specimen immediately prior to the accidental overstrain. The remaining curves show that the metal recovered its original condition within a period of 24 hours.

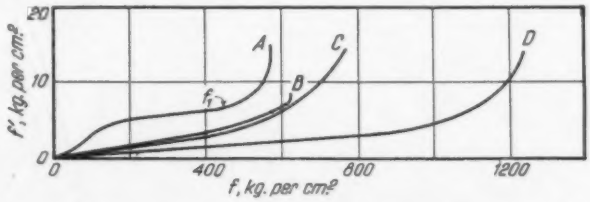

Fig. 9—Plastic Deformation and Recovery in Purified Iron.
A—Original.
B—Immediately After 180 Degrees Cold Twist.
C—20 Hours Later.
D—6 Months Later.

The next step was to determine what influence the amount of overstrain had on the curve. The result is illustrated in Fig. 8. It is seen that the slope of the main part of the curve is independent of the amount of the overstrain, varying from 7 to 36 degrees on specimens of two sizes. It will be seen that the curves are almost identical. At the end nearest the origin these curves, which are

nearly straight, appear to intersect the f axis at a stress of 100 kg/cm². This initial value of f is the f_o stress for the plastically deformed iron. If we define Φ_p as the slope of the line between f_o and f_1 we find Φ_p for this material equal to 0.03.

The curves in Fig. 9 show recovery from a cold twist of 180 degrees in hydrogen-purified iron. The slope Φ_p is here about 0.026. However, the final slope acquired after 24 hours' recovery is still far steeper than in the unpurified iron. The greatest value attained by

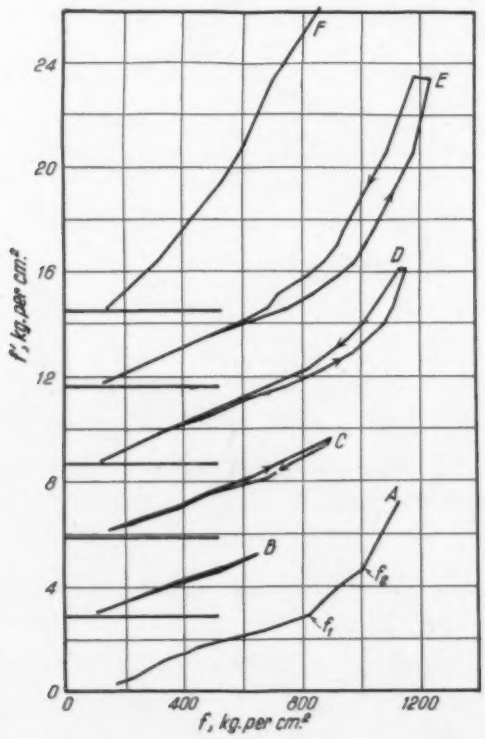

Fig. 10—Ascending and Descending Curves (0.25 per cent Carbon Steel).
A—Original.
B—C—D—E—Curves Carried to Indicated Amplitudes.
F—Same After 2,700,000 Cycles at 1200 kg/cm².

the f_1-point 24 hours after the cold work is 520 kg/cm². If a high value of internal friction and a low value of f_1 are concomitants of ductility or softness, then the purified iron remains much softer after cold work than does the unpurified; but after 6 months the iron is much altered. The main difference due to high purity is the much slower aging.

Further Properties of the f_1-Stress. Possible Existence of an f_2-Stress

The most important characteristic of the f_1 stress has yet to be described. It is as follows:

Stress cycles of lower amplitude than f_1 produce no change in the f'-f curve or any other measurable physical property of the specimen, no matter how often repeated. Stress cycles of higher amplitude than f_1 do produce changes in the f'-f curve.

These generalizations are supported by numerous experiments

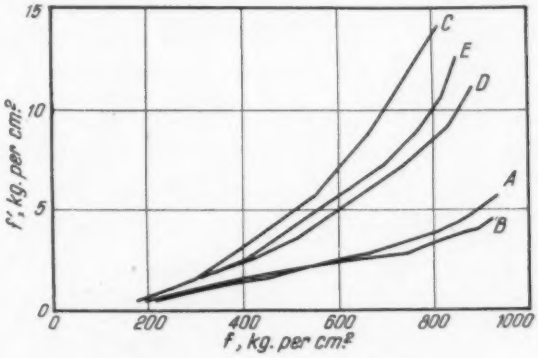

Fig. 11—0.25 Per Cent Carbon Steel.
A—Original.
B—After 5,000,000 Cycles at 700 kg/cm².
C—Same After 2,700,000 Cycles at 1000 kg/cm².
D—Same After 3,000,000 Cycles at 650 kg/cm².
E—Same After 30 Hours' Recovery.

of the author's, both on ferrous and nonferrous metals. A few of these results are selected for presentation here.

Fig. 10 gives a series of f'-f curves for normalized 0.25 per cent carbon steel, with readings taken first in ascending and then in descending order. Any displacement of the descending portion relative to the ascending is due to the effects of whatever number of stress-cycles of higher amplitude have been made in the course of taking data for the curve—perhaps 200 to 500 cycles for each plotted point. Curve (A) is the original curve (made on another similar specimen so as not to affect the remaining curves). Curve (B), which was not carried above the f_1 point, shows no difference outside the range of experimental error between ascending and descending branches. Curve (C) was carried to an amplitude above the f_1 point. The descending branch lies beneath the ascending one over a certain range, indicating a decrease in internal friction. Curve (D) was carried to a much higher amplitude. The descend-

ing branch now lies above the ascending branch and the internal friction has been increased. Curve (E) represents a still further increase over (D) due to carrying readings to still higher amplitudes. Finally curve (E) shows the effect of 2,700,000 cycles of a stress of about 1200 kg/cm² (17,000 pounds per square inch). It will be noted that curve (E) bears a strong likeness to the curves characteristic of freshly overstrained metal in Figs. 7, 8, and 9.

Again, Fig. 11 illustrates the effects of many cycles of stress above the f_1 point in 0.25 per cent carbon steel. Here curve (A) is the initial condition; curve (B) is after 5,000,000 cycles of 700 kg/cm², a stress that is very close to f_1. The result is a slight increase in the value of f_1 together with a decrease of the friction stress in the range beyond f_1. The range below f_1 is unaltered. Curve (C) gives the effects of 2,700,000 cycles of 1000 kg/cm². Curves (D) and (E) show the effects of recovery, the first during 3,000,000 cycles (about 34 hours) of a stress of 650 kg/cm², the second an additional recovery period of 30 hours under no stress. The picture presented here is so similar to the recovery of iron from plastic deformation that it seems likely that the two effects are the same. It is to be especially noted that though the treatment resulting in curve (C) reduced the value of f_1, the further cyclical stress of 650 kg/cm², *which is higher than the newly acquired* f_1, acted nevertheless as an inducement to recovery.

The data just cited point to the following conclusion: Cyclic stresses at amplitudes somewhat above f_1 result in a gradual change in the internal friction curve, the change consisting of an increase in the value of f_1 and a decrease in the internal friction. However, if the stress amplitude is too far in excess of f_1, the reverse phenomena appear; the f_1 stress is lowered and there is an increase in the internal friction.

These two observations strongly suggest the presence of still another critical stress, higher than f_1, which we shall call f_2. In fact some of our curves, e.g., curve (A) of Fig. 10, indicate the existence of such a point; but such an effect might easily be the result of the finite wall thickness of the specimen, the second break marking the point where the f_1 stress reached the inner surface; for this reason the existence of an f_2 critical stress should not be supposed from the shape of the curve without confirmatory evidence. The evidence for the existence of f_2 now seems pretty well founded, especially in the light of another experiment about to

be described. It is only to be noticed that in the light of the paragraph just above, cyclic stresses exactly equal to f_2 will cause the points f_1 and f_2 to fuse or coincide into one point. That such may be the case is shown by curves (A) and (B) of Fig. 12, curve (A) being the original and curve (B) following after.

Unsymmetrical Reversals at Stress Cycles

It is possible to modify the apparatus so that instead of varying from +f to −f, the stress may vary between s+f and s−f: in

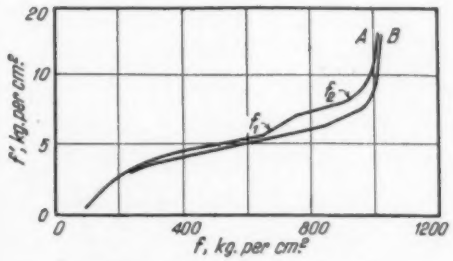

Fig. 12—Armco Iron as Rolled.
A—First Curve.
B—After Taking Data for Curve A.

other words, a steady stress s may be superposed on the cyclic stress ± f. This is accomplished by fitting a rigid steel frame about the base of the apparatus, and connecting helical steel springs to the pendulum in such a way as to introduce a controllable initial twist. It is necessary to design the springs so as to remain in tension dur-

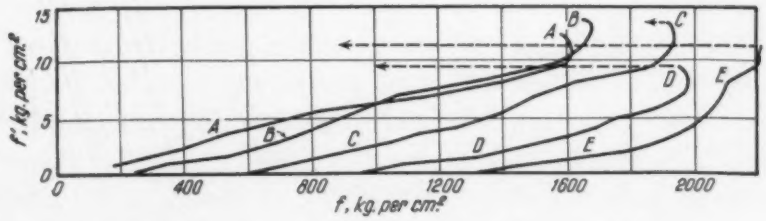

Fig. 13—0.10 Per Cent Carbon Steel with Initial Loadings.

ing the entire cycle, and to make allowance for their effect on the resonance frequency as well as their own internal friction in interpreting the results of an experiment.

Fig. 13 gives results of an experiment made on a specimen of normalized S.A.E. 1010 steel. The curves were made with varying amounts of initial stress; the plotted points are the maximum values of f. It will be noticed first that the knee characteristic of

alpha iron is present or identifiable in the higher curves. Likewise the f_1 point occurs at higher values, but not in proportion to the initial stress. As soon as the stress exceeded 1900 kg/cm² (17,000 pounds per square inch) a peculiar phenomenon began to occur. The mid-point of the oscillations began to shift; the specimen was acquiring a permanent set in compliance with the pull of the springs. Horizontal arrows are drawn from the end of each

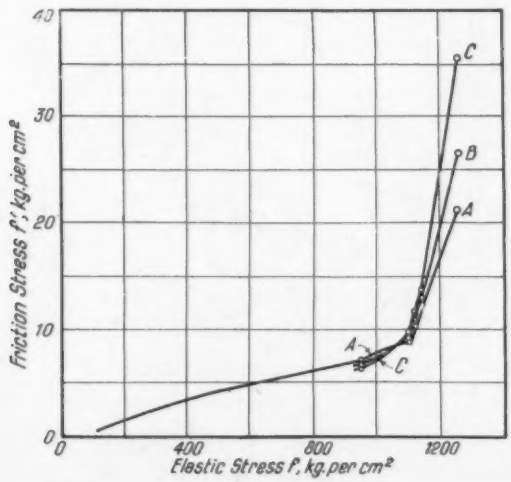

Fig. 14—0.10 Per Cent Carbon Steel (Explanation in Text).

curve indicating the amount of this relief of stress. In each case where f exceeded 1900 kg/cm² the amount of this relief exactly equalled the amount of initial stress.

Evidently the stress 1900 marks the commencement of plastic flow. This stress is definitely higher than the f_1 stress, and evidently answers the description of the f_2 stress introduced above, but is not the same as the f_2 stress obtained by symmetrical stress cycles (see below).

Still another experiment on a specimen of S.A.E. 1010 steel, normalized, is shown in Fig. 14. The manner of taking these observations was as follows: On first attaining a given stress amplitude a reading was made; then the specimen was given 5000 cycles at this amplitude and a second reading taken; then another 5000 cycles and a third reading. Then the stress amplitude was increased and the same process repeated. The three sets of points from curves labelled (A), (B) and (C). Here we have plain evidence of the two ranges of progressive change—the range be-

tween f_1 and f_2 where the internal friction is decreased by the repetitions, and the range above f_2 where it is increased. The position of f_2 is quite accurately established by these curves at a value of 1080 kg/cm² (15,400 pounds per square inch).

Tentative Account of Processes of Slip in Lower Ranges of Internal Friction

Returning again to our hypothesis of the mechanism by which internal friction occurs, we note that in all metals containing alpha iron as one phase, there is a range f_o to f_{o1} occurring at low stresses, where the slope is high. The critical stress f_o at which this starts depends on the purity and softness of the iron and appears to be almost vanishingly small for iron possessing the extreme degree of these qualities. We may, therefore, assume that this range is due to slip along a first preferred set of planes, but that if these planes are distorted by distortions of the lattice due to presence of impurities or to work hardening, the onset of slip is delayed until the shear stress attains a value f_o. As to the cause of whatever internal friction exists below f_o we advance no explanation. On first attaining f_o, only those grains having preferred planes (let us call them A-planes) lying exactly in the plane of the sheer stress are involved in the slipping process; but as f increases, more and more grains will be found to have A-planes on which the resolved component of shear stress will have the value of f_o. As more grains are involved in the slipping process, more energy will be lost per cycle, and the f′-f curve rises steeply.

Thus far the explanation seems plain enough. But now we come to the "knee" or stress f_{o1}, above which f′ increases very slowly (if at all). What can be the explanation of this phenomenon? There seems to be two possible conclusions regarding this. First it is possible that at f_{o1} the shear stress attains a value such that slip is initiated along a new set of planes. The energy lost in sliding on the new B-planes is, however, lower than that due to sliding along the A-planes, so that the dissipation of energy does not increase so fast as it did during the involvement of new A-planes. In accepting this explanation it is necessary to assume that grains wherein slip along A-planes had already commenced continue to slide along these planes, and that the B-plane sliding occurs in grains very badly oriented for A-plane slip. A second explanation is that the f_{o1} point marks the stress at which all grains have become

involved in the A-plane sliding, and that above this point no new grains are brought into the picture. Since the amount of slip is limited to one atom-diameter, there is no possible way by which the loss of energy can increase further.

At present the author cannot offer any good reason for adopting one of these explanations in preference to the other, although the second seems to be the more likely, especially in the light of the fact that in extreme cases the slope above f_{o1} seems to become vanishingly small.

At f_1 a new phenomenon makes its appearance. From whatever cause, the type of slip now in evidence results in permanent changes in the grains, a phenomenon which has not appeared in the lower ranges of stress. Whatever occurs here is of a nature such as to discourage further changes of the same kind, since it tends to raise the value of f_1 and decrease the loss of energy.

At all events the range of stress above f_1 where this hardening occurs is fairly narrow and is soon succeeded by the range above f_2 where true plastic deformation makes its appearance. The process of cyclic stress in this range has the same effect as true plastic deformation does. It changes the form of the f′-f curve throughout its length, and increases the friction stresses throughout the whole range.

Without doubt the intragranular slipping which is now taking place is no longer the reversible jump of a single atom diameter, but a displacement of many diameters, accompanied by a rotation or strain of the grain in which it occurs, of such a nature that the reverse displacement which may be expected to follow when the stress is reversed is no longer in the same direction. In this way the grains adjacent to the one just affected are now put in an initially strained condition such that the next cycle of stress involves still other grains in the progressive breakdown of structure. The final effect seems to be the establishment of paths of easy slip traversing the structure of the metal. The lapse of time, however, seems to enable the crystals to rearrange themselves so as to interrupt these paths, unless the stress-amplitude is maintained at such a value as to break down the renewed resistance of the grains as fast as it is developed.

Internal Friction in Carbon Steels

A series of experiments was performed on hardened and un-

hardened steels according to the following table:

Steel	Per Cent Carbon Content	Heat Treatment Hardening Degrees Fahr.	Heat Treatment Drawing Degrees Fahr.
A	0.27	1600 in water	1100
B	0.51	1500 in oil	1100
C	0.87	1455 in oil	1100
D	1.17	1650 in oil	1100

The resulting internal friction curves are presented in Figs. 15 and 16. These data were taken prior to adopting the vacuum tube method of driving the pendulum. The individual points are not, therefore, as trustworthy as most of the others in this paper. The

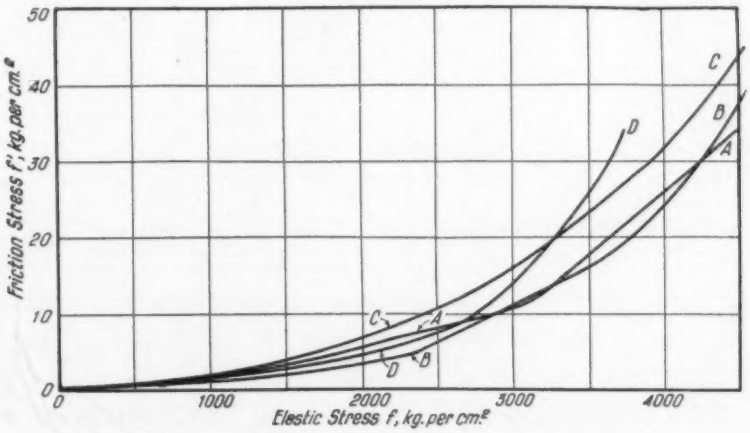

Fig. 15—Quenched Carbon Steels (See Text).

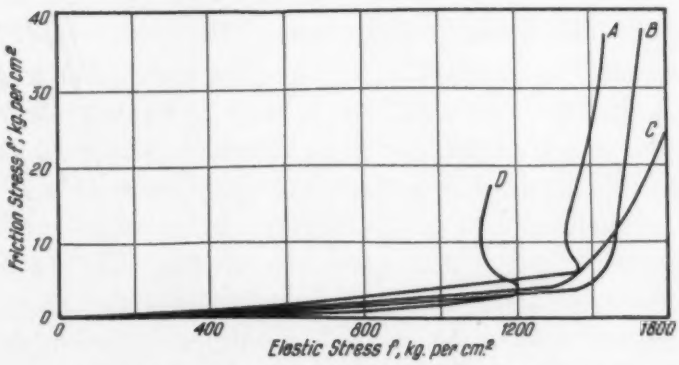

Fig. 16—Quenched and Drawn Carbon Steels (See Text).

reader will note in these curves the almost complete absence of the alpha iron knee in those specimens which have been hardened; likewise the lack of any sharp indication of other critical points on the curves. The former effect is undoubtedly due to the "keying" effect

of lattice distortion brought about by hardening; the latter, to internal stresses, as mentioned previously.

Some Ferrous Alloys. In Fig. 17 are presented internal friction curves for a "free-machining" stainless iron containing carbon 0.08 per cent, chromium 13.5 per cent, with presumable presence of 0.29

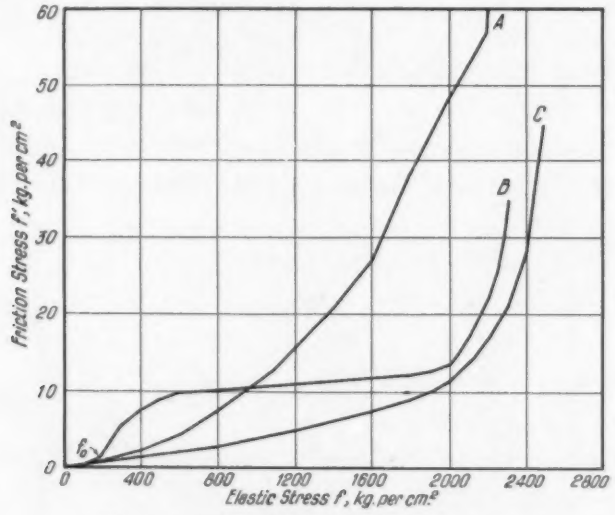

Fig. 17—"Free Machining" Stainless Iron.
A—Cold Drawn as Delivered.
B—After Annealing.
C—After Quenching.

per cent of zirconium sulphide inclusions. This material was received in the form of cold drawn stock intended for automatic screw-machine use. In this condition its f′-f curve is curve (A) in the figure. The interesting feature of this curve is its steepness at all amplitudes. Curve (B) is the same material after a strain-relieving anneal. In this condition it shows the characteristic alpha iron knee, but the discontinuity at f_1 is smoothed out, doubtless because of the distorted solid solution lattice. Curve (C) is the same steel after quenching from 1825 degrees Fahr. in oil and drawing at 700 degrees Fahr. The quench-hardening has produced the smoothed out curve characteristic of carbon steels similarly treated, and the internal friction is very low compared with curve (A) although the f_1 stress cannot be much different for the two conditions.

Fig. 18 shows curves for (A) a 38 per cent nickel steel in a work-hardened condition, and (B) a hot-rolled 18-8 steel. All these represent austenitic solid solutions, and the alpha iron knee is absent. The effect of the work-hardening on the 38 per cent nickel

steel is extraordinary. It shows no evidence of the high internal friction found in work-hardened alpha solid solutions.

Internal Friction a Desirable Physical Property

There are a few applications of metals where internal friction is to be avoided. Such purposes would include piano strings, tun-

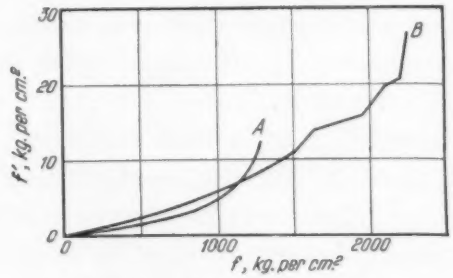

Fig. 18—Austenitic Steels.
A—38 Per Cent Nickel Steel.
B—18-8 Stainless Steel.

ing forks, bells, hair springs for clocks and watches, and reeds of frequency meters.

For most engineering purposes, however, the loss of energy due to internal friction in members transmitting power is rather small unless the member is unusually large. Naturally it only appears in connecting-rods or other parts carrying alternating stresses. In a piston rod or connecting rod of length 1 transmitting an alternating motion of amplitude r, the fraction of power lost is $\pi\ 1/\Phi\ r$, where Φ is the ratio f'/f for the stress range in which the material is working. This fraction will be of the order of 0.1 to 1 per cent in most cases.

There are many other cases, where internal friction is an exceedingly desirable property. Consider for example a long shaft transmitting torque from an engine to a propeller or other power-consuming device. The torque is on the whole an unvarying one so that actual loss of energy is not an important consideration; but superposed on the steady torque there are periodic fluctuations arising from piston impulses, turbine blading, gear imperfections or other causes. If these fluctuations agree in frequency with some natural elastic frequency of the mechanical system, they will build up elastic vibrations, the amplitude of which is only limited by internal friction in the metal and such external friction as may be introduced by bearings.

That these forced vibrations may easily be destructive is known to every engineer. They are of particularly serious importance when they occur at speeds of normal running of machinery, though they may be troublesome even when encountered only during starting up or stopping. For example, it has happened that such a critical vibration absolutely forbade the operation of a naval vessel at a certain speed not far from her normal cruising speed. Such a defect, bad enough in a commercial ship, may be simply not permissible in a naval vessel whose duties require her to steam in close formations at prescribed speeds.

One method of eliminating critical vibrations is to design the machine so that all its natural frequencies are remote from any working speed. This may involve very uneconomical proportions and distributions of material. Another method is, of course, to use bearings that act as brakes. The disadvantage of this procedure is that it exacts the same toll of energy from the useful movement of the engine as it does from the useless vibration. The third, and logical procedure, is to utilize a material possessing high internal friction for any long shaft or any other large member that carries a steady load but is also subject to danger from vibration. The same end may be accomplished, of course, by introducing special couplings, in the shaft or other member, designed to damp out vibrations; but the use of such devices may be undesirable on account of expense, bulk, and lack of permanency.

To cite an example, the curves of Fig. 17 are offered. At the same stress of 1600 kg/cm^2 (22,700 pounds per square inch) the strain-hardened material would permit vibrations only of one fifth the amplitude of the quench-hardened and about one-fifteenth that of the annealed material. (This is based on the assumption that unsymmetrical stress-cycles about a certain initial stress give a value of Φ about equal to the slope of the f′-f curve at a stress amplitude equal to the initial stress. There is evidence, not shown here, that this is approximately true).

Internal Friction and Fatigue

Up to this point the author has avoided reference to any relation between internal friction and the endurance properties of a metal. There can be little doubt that such a connection exists, but it is likewise true that there is no such easy operation as finding the endur-

ance limit by identifying it with one of the critical points of the f′-f curve.

There is one fact in connection with this whole matter, which stands out with some prominence. In strain-free iron or steel, the f_1 stress is clearly marked, and it is certain that cyclic stresses of a smaller amplitude than f_1 leave the metal unchanged, no matter how often repeated. It is therefore inconceivable that stress cycles within this range can be productive of failure, for we should certainly not look for failure to occur in the absence of changes in the metal to presage it.

As already noted, heat treated or otherwise hardened material presents a much less simple picture, and it is difficult to identify the f_1 point with certainty. Moreover, even if the stress amplitude exceeds f_1 there is no certainty that the progressive changes induced thereby are destined to cause the metal to fail. They may, on the contrary, strengthen it enough to resist failure. Indeed Gough[10] has advanced the proposition that resistance to fatigue is always a property acquired during the progress of cyclic stress. The author does not agree to this extreme view, in the light of his own experiments, but does not doubt that changes wrought in the metal during the first few thousand cycles of fatigue may be responsible for part of the endurance of the metal. There is not even any proof in any of the author's experiments that the plastic yielding above the f_2 point is a sufficient cause for fatigue failure. It is hoped at a future date to be able to report some definite findings on this important branch of the subject. At present, beyond the remarks made above, the author has nothing of value to present.

Table of Values of Φ

To conclude the paper a few values of initial coefficients of internal friction and the coefficients at the f_1 point are included. After what has already been said here, it is unnecessary to remind the reader of the great variability of these coefficients, subject to variations in mechanical history and heat treatment. In order to convert these to coefficients for direct tension and compression, a rough and ready method is to multiply by 0.85. The values listed include some for nonferrous metals.

The author takes this opportunity of thanking Albert Smith, of the Johns Hopkins University, and J. D. Beardsley of this laboratory,

[10] H. J. Gough, *Engineering*, March 2, 1928.

for doing much of the actual work of operating the apparatus and working up data.

Values of Coefficients of Internal Friction Calculated for $f = 0$ and for $f = f_1$

Material	Condition	(Initial Value)	f_1	(f_1'/f_1)
Armco Iron	As-rolled	<0.005	800	0.0045
Steel, 0.27 per cent carbon	As-rolled	<0.0050		
Steel, 0.27 per cent carbon	Quenched	<0.0009	2100 ?	0.0030
Steel, 0.27 per cent carbon	Drawn 600 degrees Cent.	<0.0008	1260	0.0025
Steel, 0.51 per cent carbon	As-rolled	<0.0016		
Steel, 0.51 per cent carbon	Quenched	<0.0013	1660 ?	0.0014
Steel, 0.51 per cent carbon	Drawn 600 degrees Cent.	<0.0004	920	0.0025
Steel, 0.87 per cent carbon	As-rolled	<0.0068		
Steel, 0.87 per cent carbon	Quenched	<0.0020		
Steel, 0.87 per cent carbon	Drawn 600 degrees Cent.	<0.0010	1060	0.0026
Steel, 1.17 per cent carbon	Quenched	<0.0012	2000 ?	0.0016
Steel, 1.17 per cent carbon	Drawn 600 degrees Cent.	<0.0004	800	0.0010
Free Machining Stainless Iron	Cold drawn	<0.005	1600 ?	0.0170
Free Machining Stainless Iron	Annealed	<0.007	1800	0.0068
Free Machining Stainless Iron	Quenched	<0.0028	1800	0.0050
Duralumin	Aged	<0.0039	1400	0.0061
Cartridge Brass	Cold-worked	<0.0023	500	0.0028
Cartridge Brass	Annealed	<0.0036	400	0.0050

DISCUSSION

Written Discussion: By G. R. Brophy, General Electric Co., Research Laboratories, Schenectady, N. Y.

Mr. Canfield's results are of interest and importance in that he points out, I believe for the first time, that the damping or internal friction curves of annealed steel contain critical stress points. It may be possible, through these points, to arrive at a correlation between this interesting property of damping, and the other more commonly known physical properties.

These critical points can only be shown by the use of tubular test specimens which will give more nearly the true internal friction for a given stress, whereas with solid bars used in the Föppl-Pertz method and that used by Kimball, the average friction over the cross section of the bar is plotted against the maximum fiber stress. This consideration may account for the fact that Canfield's results are usually twice, and in some cases four times those of Föppl, Van Heydekampf and Kimball for, presumably, the same material.

The relation between the author's results and those of the writer's mentioned may be developed as follows:

$$\frac{P}{2} = \delta = \frac{W'}{W}$$

P = Föppl's specific damping capacity

δ = Kimball's log. decrement

$W = f^2/2E$ Canfield's equation No. 1

$$W' = \frac{4ff'}{E} \text{ Canfield's equation No. 2}$$

Therefore

$$\frac{P}{2} = \delta = 4\frac{f'}{f}$$

It should be emphasized that slight differences in composition, thermal and mechanical histories of the respective test pieces will influence the results so a comparison should be made cautiously.

Another possibility is that Canfield's high results are due to losses in his equipment. This is suggested by the rigid concrete support for his test specimens.

Referring to Fig. 16 which shows the f'-f curves for quenched and drawn carbon steel, it appears that curves A and D may represent impossible conditions. In the stress range just above 1100 kilograms per square centimeter for each stress there are three values for internal friction. These curves indicate also that the amplitude of vibration decreases as the energy input increases. An explanation of these points would be appreciated.

It has been the writer's experience that cold work, in common with other hardening treatments, decreases the internal friction, at least in the stress range in excess of 5000 pounds per square inch. This applies to steels which have been heavily cold-worked. (25-30 per cent reduction.)

Mr. Canfield logically suggests, as do Föppl and Von Heydekampf, that there is a correlation between internal friction and fatigue properties, and especially where notches influence the endurance limit. Tests by the writer, which are to be published shortly, on five steels each in three conditions of heat treatment, indicate that there is no relation between the endurance limits of notched and unnotched fatigue specimens and the internal friction. Nor does the reduction of endurance limit due to the notch bear any relation.

These results were most disappointing; so much so, that additional tests are being carried out to determine whether there is a general relation and that the choice of materials used was unfortunate.

Author's Reply to Discussion

As pointed out by Mr. Brophy, the author's values of internal friction are higher than those reported by others; it is possible that a portion of this loss is due to losses in the rigid concrete base of the machine, as suggested by Mr. Brophy. However, this loss cannot be greater than the smallest value of internal friction ever recorded on this apparatus; and some of the values obtained have been quite low. For instance, we have recorded values of Φ as low as 0.0007 at a stress of 1500 kilograms per square centimeter.

For many purposes of the paper under discussion, however, it is the changes and differences of internal friction rather than absolute values that are of interest; and these observations are, of course, unaffected by the possible losses in the apparatus.

It will be noted, that most f'-f curves show a tendency to become tangent

to the f-axis near the origin; thus in a solid specimen where part of the metal passes through a small stress-cycle the apparent slope of the curve will be smaller; and thus, as pointed out in the paper and mentioned by Mr. Brophy, solid specimens will tend to exhibit a spuriously low damping coefficient. The author feels that this accounts for a considerable proportion of the discrepancy between his results and those of others.

Mr. Brophy's conclusion that cold work and other hardening treatments decrease the internal friction in steels is the same as that of the author, and is true of other metals as well. Part of this effect is due to the disappearance of the "knee" in the f′-f curve of the alpha iron, and part to a raising of the f_1 stress. In quenched and tempered steels there is also a true decrease of slope. During the progress of precipitation hardening in duralumin there is likewise a marked diminution in slope of the curve below f_1, as well as an increase in the value of f_1.

As opportunity offers, the author intends to modify his apparatus so as to utilize the double pendulum principle originated by Föppl, and thus eliminate the objectionable rigid base critized by Mr. Brophy.

The comment in regard to Fig. 16 is answered by saying that the curve represents a succession of readings. The inflexion of the curve is due to changes in properties of the steel during the course of the experiment.

Referring to Mr. Brophy's summary of the relations between constants expressing internal friction used by Föppl, Kimball, and the author, it may be permissible to summarize the latter's views in defense of his own terminology, as follows:

(1) Insofar as energy-loss is proportional to elastic energy (constant logarithmic decrement) then f′ is proportional to f, and in fact $f' = \Phi f$, where Φ is the author's proposed coefficient. This coefficient has all the advantages of a nondimensional constant, being independent of systems of units.

(2) When, as in the majority of cases, f′ is not proportional to f,, then the curve f′ versus f illustrates any departure from this law much more graphically than F versus f, for instance; at the same time it expresses results in terms of stresses, which are familiar terms for most engineers.

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